STANDARD OPERATING PROCEDURE FOR VOLATILE ORGANICS COMPOUNDS AND VOLATILE PETROLEUM HYDROCARBONS USING EPA METHOD 624 AND SW-846 METHOD 8260B

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This SOP is effective upon signed approval by the following:

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DISCLAIMER: This SOP has been developed for use at the Microbac Laboratories, Merrillville, Indiana facility. It is intended for use by trained analysts. As written, this SOP may not be specifically applicable to the activities of other organizations.

Last Review Date:
No Changes Needed
Approved By:

1.0 TABLE OF CONTENTS

2.0 SCOPE AND APPLICATION

2.1 This is a GC/MS procedure for the determination of volatile organic compounds. This procedure is applicable to the analysis of aqueous, non-aqueous liquid and solid matrix samples. The applicable compounds and their routine reporting limits are listed in the applicable test codes in LIMS. This procedure can also be used to determine the concentration of Volatile Petroleum Hydrocarbons, specifically gasoline or its individual components, which can be reported as Gasoline Range Organics.

2.2 The different and distinct autosampler units are employed as part of this procedure.

- The Tekmar 2016 autosampler is used to analyze samples according to SW-846 Method 5030B, which is a purge-and-trap procedure for aqueous and water miscible liquid samples. In certain applications, the 2016ALS and Method 5030B may be used for the analysis of soil samples as well.

- The Solatek 72 autosampler is used to analyze samples according to SW-846 Method 5035, which utilizes a closed-system purge-and-trap process for the analysis of volatile organic compounds (VOCs) in solid materials (e.g., soils, sediments, and solid waste). The Solateks can also be used for the analysis of water samples.

2.3 While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes.

3.0 SUMMARY

3.1 Samples are loaded onto an autosampler and the volatile compounds are introduced into the gas chromatograph using the purge-and-trap technique. The analytes are directly injected onto the capillary column of the GC. The column is temperature programmed to separate the analytes that are detected, using ion counts, with a mass spectrometer interfaced to a gas chromatograph. Target ions are extracted from the total ion count to identify target compounds.

3.2 Water samples are collected in glass vials with zero headspace. When using the Tekmar 2016, an aliquot of sample (typically 5-ml or 25-ml) is transferred into a test tube using a gas-tight syringe. When using the Solatek, an aliquot of sample (typically 5-ml or 25-ml) is withdrawn directly from the sample vial.

3.3 Soil samples are collected in a variety of sample containers dependent upon the application. When using the Tekmar 2016 for low level solid samples, 5g of sample is weighed into a test tube and 5-ml of lab pure water added prior to loading the tube onto the autosampler. When using the Solatek for low level solid samples, 5g of sample is added to a vial (either during collection or at the lab), which is loaded onto the autosampler for analysis. For medium and high level solid samples, 5g of

sample is extracted with 5-ml methanol and a portion of this extract is diluted with lab pure water, purged and analyzed.

3.4 The calibration range for most target analytes using 5ml or 5g of sample is 5-200 ppb.

3.5 This procedure is based on the reference methods listed in section 17 of this document. This procedure contains no significant deviations from the reference methods.

4.0 DEFINITIONS

4.1 A list of definitions is in the Quality Assurance Plan. In addition to the terms defined in the QAP.

5.0 INTERFERENCES

5.1 Chemical interference is minimized through the use of ion counts and internal standards.

5.2 Occasionally, samples may foam while being purged. This problem can be corrected through dilution or the use of a silicone-based anti-foaming agent.

5.3 Contamination may occur from impurities in the purge gas, carryover from high-level samples or environmental contamination resulting from the introduction of target analytes into the lab. Method blanks are used to verify that the system is clean and suitable for analysis. Analyzing additional blanks and/or baking out the column between analyses can eliminate carryover contamination.

6.0 SAFETY

6.1 Consult the current revision of the Chemical Hygiene Plan. Requirements for the use of personal protective equipment (e.g. safety glasses, lab coats, gloves) as well as other area-specific safety requirements (e.g. gas cylinders) and MSDS sheets are addressed in the CHP.

7.0 EQUIPMENT AND SUPPLIES

The following is a list of materials needed to perform the steps of this procedure as written. See the reference method(s) for equipment and supply specifications.

7.1 All volumetric glassware used shall be ASTM Class A. Glass microliter syringes are considered Class A provided they provided they come with a certificate attesting to the accuracy of the syringe. Syringes without vendor certification are considered Class B glassware. Class B glassware must be verified for accuracy on an annual basis and labeled with an appropriate correction.

7.2 GC/MS System consisting of the following:

7.2.1 HP 5890 Series II Gas Chromatograph

7.2.2 Tekmar SOLAtek® 72 autosampler

7.2.3 Tekmar 2016 ALS with disposable 25-ml autosampler tubes

7.2.4 Tekmar LSC 2000, LSC3000 or LSC3100 purge and trap concentrator

7.2.5 Vocarb 3000 Trap: Supelco Purge Trap K catalog # 24920-U. Equivalent products from other vendors may be used.

7.2.6 HP 5970, 5971A or 5972 Mass Selective Detector

7.2.7 Chromatographic column: J&W Scientific DB-624 catalog # 128-1324: dimensions length 25m, ID 0.2mm, film thickness 1.12um; or Phenomenex Zebron ZB-624 catalog # 7HG-G005-27: dimensions length 30m, ID 0.25mm, film thickness 1.4um. Equivalent products from other vendors may be used.

7.3 Computer with MS Chemstation software, monitor, and printer

7.4 Various gas-tight syringes including 10, 25 and 50-ul

7.5 5-ml gas-tight syringes with Luer-lock tip

7.6 2-ml autosampler vials with crimp tops or screw caps

7.7 1-ml mini-inert vessels with caps

7.8 40-ml glass VOA vials with Teflon lined screw cap septa

7.9 Top loading balance capable of ± 0.01g sensitivity

7.10 Disposable glass pipettes

8.0 REAGENTS AND STANDARDS

8.1 All reagents used must be analytical reagent (AR) grade or higher. All standards must be traceable to NIST, when available. Certificates of traceability must be obtained from the manufacturer. All reagents and standards must be documented in the appropriate preparation logbook. Refer to the requirements in the Labeling of Standards, Reagents, Digestates and Extracts SOP.

8.2 Reagents

All reagents are stored in the VOA lab unless otherwise noted.

8.2.1 Lab pure water (DI water): Analyte free water is prepared as described in the Quality Assurance Plan supplemented with additional carbon filtration after the general treatment. DI water may be obtained from the designated tap in the VOA lab.

8.2.2 Methanol, purge and trap grade

8.2.3 Sand: Prepare by baking in an oven at >70°C for a minimum of 3-hours.

8.3 Standards

All standards are stored in the standards freezer in the VOA lab unless otherwise instructed by the manufacturer's recommendation. Expiration of prepared standards must be performed in accordance with the Labeling of Standards, Reagents, Digestates and Extracts SOP.

NOTE: The following solutions are used to prepare standards for the analysis of individual compounds. Refer to the last step in this standards section for the preparation of standards for "gasoline".

8.3.1 Stock Internal Standard (I.S.), 2000 ug/ml each in methanol. Equivalent products from other vendors may be used.

VENDOR	CAT #	COMPOUNDS
Accustandard	M-8260A/B-IS-10X	Chlorobenzene-d5; 1,4-Dichlorobenzene-d5; Fluorobenzene

8.3.2 Stock Surrogate (SURR) Standard, 2000 ug/ml each in methanol. Equivalent products from other vendors may be used.

VENDOR	CAT #	COMPOUNDS
Accustandard	M-8260A/B-SS-10X	4-Bromofluorobenzene; Dibromofluoromethane; 1,2-Dichloroethane-d5; Toluene-d8

8.3.3 Working I.S./SURR Solution, 50 ug/ml each: In a 10-ml volumetric flask, dilute 250-ul of Stock I.S. and Stock SURR standards to the mark with methanol. Prepare new solution at a minimum of every 6-months. The addition of 5-ul of this solution to 5-ml of sample yields a concentration of 50 ug/l.

8.3.4 Stock Calibration Standards, 2000 ug/ml each (unless otherwise noted) in methanol. Equivalent products from other vendors may be used.

GROUP	VENDOR	CAT #	COMPOUNDS
Non-gases	Accustandard	M-502A-R2-10X	See Table in Section 18.0
8260 Cal Mix 2	Supelco	46831-U	Acetone; 2-Butanone; Carbon disulfide; 2-Chloroethylvinyl ether; 2-Hexanone; Iodomethane; 4-Methyl-2-pentanone; Vinyl acetate
Gases	Accustandard	M-502B-10X	Bromomethane; Chloroethane; Chloromethane; Dichlorodifluoromethane; Trichlorofluoromethane; Vinyl chloride
	Accustandard	M-603-10X	Acrolein; Acrylonitrile @ 10,000 ug/ml each
	Accustandard	APP-9-005-10X	Acetonitrile @ 1000 ug/ml
	Accustandard	S-078-10X	Methyl-t-butyl ether

8.3.5 Intermediate Calibration Standards: In separate 1-ml volumetric flasks, prepare the following dilutions of the stock calibration standards with methanol. Prepare new solutions at a minimum of every 6-months with the exception of the Gases, which must be prepared on a weekly basis.

	Group	Vol. Stock Cal. Std., ul	Final Conc., ug/ml
1	Non-gases and "8260 Mix 2"	25 each	50
2	Gases	25	50
3	Acrolein; Acrylonitrile	50 each	500
4	Acetonitrile	500	500
5	Methyl-t-butyl ether	25	50

8.3.6 Working Calibration Standards (Linearity, ICAL):

Water Linearity SOLATEK - In separate 50-ml volumetric flasks, prepare the following dilutions with lab pure water. Transfer the prepared standards to 40-ml VOA vials leaving zero headspace.

Linearity Standard #	Vol. Inter. Cal. Std, ul	Final Conc. ug/l
1	5	5
2	10	10
3	20	20
4	50	50
5	100	100
6	200	200

Soil Linearity SOLATEK – Using a 5.0-ml syringe, individually prepare the following dilutions with 5.0-ml lab pure water. Transfer the prepared standards to 40-ml VOA vials for analysis.

Linearity Standard #	Vol. Inter. Cal. Std, ul	Final Conc. Ug/l
1	1 (V_f = 10ml)	5
2	1	10
3	2	20
4	5	50
5	10	100
6	20	200

Water/Soil Linearity TEKMAR 2016 - In a 5-ml syringe, individually prepare the following dilutions with 5.0-ml lab pure water and 5-uL of the working ISTD/SURR solution. Transfer the prepared standards to separate ALS tubes for analysis.

Linearity Standard #	Vol. Inter. Cal. Std, ul	Final Conc. ug/l
1	1 (V_f = 10ml)	5
2	1	10
3	2	20
4	5	50
5	10	100
6	20	200

8.3.7 Working Calibration Verification (CCV) Standard, 50 ug/l each: Use the Linearity Standard #4.

8.3.8 Stock Verification/Spike Standards, 2000 ug/ml each (unless otherwise noted) in methanol. Equivalent products from other vendors may be used.

GROUP	VENDOR	CAT #	COMPOUNDS
Non-gases	Supelco	502111	See Table in Section 18.0
Gases	Supelco	48799-U	Bromomethane; Chloroethane; Chloromethane; Dichlorodifluoromethane; Trichlorofluoromethane; Vinyl chloride
8240B Cal Mix 2	Supelco	47364	Acetone, Acetonitrile, Acrylonitrile, 2-Butanone, 2-Hexanone, 4-methyl-2-pentanone
MTBE	Restek	30402	Methyl-t-butyl ether
Carbon Disulfide	Restek	30258	Carbon Disulfide
2-CEVE	Restek	30265	2-Chloroethylvinyl ether
Vinyl Acetate	Restek	30216	Vinyl Acetate

8.3.9 Intermediate Verification/Spike Standards: In separate volumetric flasks, prepare the following four standard by diluting the stock calibration verification standards with methanol. Prepare new solutions at a minimum of every 6-months with the exception of the Gases, which must be prepared on a weekly basis.

STD	VENDOR & CATALOG #	Vol. Stock Verif. Std., ul	Final Vol., ml	Final Conc., ug/ml
Check Std #1	Supleco 502111	25	1.0	50
Gases	Supelco 48799-U	25	1.0	50
Check Std #2	Supleco 47364	25	1.0	50
Check Std #3	Restek 30265, 30216, 30402, 30258	25 each	1.0	50

8.3.10 Initial Calibration Verification (ICV) Standard, 50 ug/l:

For SOLATEK Water Calibrations – In a 50-ml volumetric flask, dilute 50-ul of each intermediate verification/spike standard to the mark with lab pure water. Transfer to a 40-ml VOA vial leaving zero headspace.

For SOLATEK Soil Calibrations – In a 5.0-ml syringe, add 5.0-ul of each intermediate verification/spike standard to 5.0-ml lab pure water. Transfer to a 40-ml VOA vial for analysis.

For TEKMAR 2016 Calibrations – In a 5.0-ml syringe, add 5.0-ul of each intermediate verification/spike standard as well as 5-ul of the Working I.S./SURR solution to 5.0-ml lab pure water. Transfer to a 25-ml autosampler tube for analysis.

8.3.11 Laboratory Control Sample (LCS):

For SOLATEK Water Calibrations – In a 50-ml volumetric flask, add 20-ul of each intermediate verification/spike standard and dilute to the mark with lab pure water. Transfer to a 40-ml VOA vial leaving zero headspace. This prepares a LCS of 20 ug/l each.

For SOLATEK Soil Calibrations – In a 5.0-ml syringe, add 5.0-ul of each intermediate verification/spike standard to 5.0-ml of lab pure water. Transfer to a 40-ml VOA vial containing 5g of sand. This prepares a LCS of 50 ug/l each.

For TEKMAR 2016 Water Calibrations – In a 5.0-ml syringe, add 2.0-ul of each intermediate verification/spike standard as well as 5-ul of the Working I.S./SURR solution to 5.0-ml lab pure water. Transfer to a 25-ml autosampler tube. This prepares a LCS of 20 ug/l each.

For TEKMAR 2016 Soil Calibrations – In a 5.0-ml syringe, add 5.0-ul of each intermediate verification/spike standard as well as 5-ul of the Working I.S./SURR solution to 5.0-ml lab pure water. Transfer to a 25-ml autosampler tube. This prepares a LCS of 50 ug/l each.

8.3.12 Matrix Spike / Matrix Spike Duplicate (MS/MSD):

For SOLATEK Water Analyses – In a 25-ml volumetric flask, measure 25-ml of sample and add 25-ul of each intermediate verification/spike standard to prepare a MS at 50 ug/l (Method 8260B); use 10-ul of each spike standard to prepare a MS at 20 ug/l (Method 624).

For SOLATEK Soil analyses – To 5g of sample in a VOA vial, add 5.0-ul each intermediate verification/spike standard to prepare a MS at 50 ug/Kg.

For TEKMAR 2016 Water Analyses – To 5.0-ml sample in 5-ml syringe, add 5.0-ul of each intermediate verification/spike standard as well as 5-ul of the Working I.S./SURR solution to prepare a MS at 50 ug/l (Method 8260B); use 2.0-ul of each spike standard to prepare a MS at 20 ug/l (Method 624). Transfer the spiked sample to a 25-ml autosampler tube for analysis.

For TEKMAR 2016 Soil analyses – In a 5.0-ml syringe, add 5.0-ul of each intermediate verification/spike standard as well as 5-ul of the Working I.S./SURR solution to 5.0-ml lab pure water. Transfer the spike to a 25-ml auosampler tube containing 5g sample. This prepares a MS at 50 ug/Kg.

8.3.13 Method Blank (MBLK): Lab pure water is used for the MBLK associated with the analysis of water and methanol extracted samples. 5g of sand is used for the MBLK associated with the analysis of solid samples. The MBLK must be spiked with 5-ul of the Working I.S./SURR solution.

GASOLINE STANDARDS

8.3.14 Stock Gasoline Calibration Standard: Restek catalog #030206 contains unleaded gasoline at 50,000 ug/ml in methanol. Equivalent products from other vendors may be used.

8.3.15 Working Gasoline Calibration Standard, 2500 ug/ml: In a 1-ml volumetric flask, dilute 50-ul of the stock gasoline calibration standard to the mark with methanol.

8.3.16 Working Calibration Standards (Linearity, ICAL):

Water Linearity SOLATEK - In separate 50-ml volumetric flasks, prepare the following dilutions with lab pure water. Transfer the prepared standards to 40-ml VOA vials leaving zero headspace.

Linearity Standard #	Vol. Working Gas Cal. Std, ul	Final Conc. ug/l
1	4	250
2	10	500
3	20	1000
4	30	2500
5	40	5000

Soil Linearity SOLATEK – Using a 5.0-ml syringe, individually prepare the following dilutions with 5.0-ml lab pure water. Transfer the prepared standards to 40-ml VOA vials for analysis.

Linearity Standard #	Vol. Working Gas Cal. Std, ul	Final Conc. ug/Kg
1	0.5 (V_f = 10ml)	250
2	1	500
3	2	1000
4	5	2500
5	10	5000

Soil Linearity TEKMAR 2016 – Using a 5.0-ml syringe, individually prepare the following dilutions with 5.0-ml lab pure water and 5-uL of the working ISTD/SURR solution. Transfer the prepared standards to separate ALS tubes for analysis.

Linearity Standard #	Vol. Working Gas Cal. Std, ul	Final Conc. ug/Kg
1	0.5 (V_f = 10ml)	250
2	1	500
3	2	1000
4	5	2500
5	10	5000

8.3.17 Stock Gasoline Verification Standard: Accustandard catalog #GA-001-40X contains unleaded gasoline at 20,000 ug/ml in methanol. Equivalent products from other vendors may be used.

8.3.18 Working Gasoline Verification Standard, 2500 ug/ml: In a 1-ml volumetric flask, dilute 125-ul of the stock gasoline verification standard to the mark with methanol.

8.3.19 Initial Calibration Verification (ICV) Standard, 1000 ug/l:

For SOLATEK Water Calibrations – In a 50-ml volumetric flask, dilute 20-ul of the working gasoline verification standard to the mark with lab pure water. Transfer to a 40-ml VOA vial leaving zero headspace.

For SOLATEK Soil Calibrations – In a 5.0-ml syringe, add 2.0-ul of the working gasoline verification standard to 5.0-ml lab pure water. Transfer to a 40-ml VOA vial for analysis.

For TEKMAR 2016 Calibrations – In a 5.0-ml syringe, add 2.0-ul of the working gasoline verification standard as well as 5-ul of the Working I.S./SURR solution to 5.0-ml lab pure water. Transfer to a 25-ml autosampler tube for analysis.

9.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

9.1 The client or other trained personnel collect samples. Samples received at the laboratory are considered representative unless otherwise noted. Water samples should be dechlorinated prior to acidification. This is a sample collection activity that must be performed in the field.

9.2 Water samples should be collected in a 40-ml glass vial with a Teflon lined lid (VOA vial) leaving zero headspace. Preservation consists of HCl to pH < 2 and storage in the range of 0.1-6°C. Samples are stored in the dedicated VOA coolers and analysis must be performed within the maximum allowable hold time of 14-days from collection for acid preserved water samples.

9.2.1 The analyst must measure the pH after sample analysis has been performed. The result of these checks is noted on the injection log. Any sample not meeting the requirement of pH < 2 must be qualified in a Case Narrative to the client.

9.2.2 NOTE: 2-Chloroethyl vinyl ether and Acrolein will degrade with acidification.

9.2.3 Based on the data reported in section 9.3 of Method 624, unpreserved samples should be analyzed within 7-days from collection.

9.3 Soil samples should be collected according to the specifications described below. The collection steps include the preservation technique.

9.3.1 Method 5035: All samples received for analysis in strict accordance with Method 5035 must be chemically preserved with sodium bisulfate ($NaHSO_4$) or methanol and retained at 4°C until analysis. The maximum allowable hold time for bisulfate preserved samples is 14-days from collection.

9.3.1.1 Method 5035-IN: Samples received for programs that allow freezing as an alternative to the chemical preservation (e.g. Indiana) must be frozen at -12 ± 2°C within 24-hours of receipt at the lab to inhibit biodegradation. This thermal preservation technique provides for a maximum hold time of 7-days from collection. Without the thermal preservation (i.e. freezing), samples must be analyzed within 48-hours of collection. Samples stored at 4°C are retained in the dedicated VOA cooler and samples stored at –12°C are retained in the organics freezer.

9.3.1.2 Low level samples. At the time of sample collection, 5g of sample are placed into a pre-weighed VOA vial. The vials are sealed, chilled to 4°C, and must be shipped by the client for receipt within 48-hours of collection. Upon receipt, the vials are re-weighed to obtain the weight of sample, which is recorded in the VOA Soil Preparation Logbook (copy attached).

9.3.1.3 Medium/High level samples. At the time of sample collection, 5g of sample are placed into a pre-weighed VOA vial containing 5-ml of purge-and-trap grade methanol. The vials are sealed, chilled to 4°C, and shipped to the laboratory. Upon receipt, the vials are re-weighed to obtain the weight of sample, which is recorded in the VOA Soil Preparation Logbook.

9.3.1.4 Field-unpreserved samples. The sample is collected in an air-tight storage container. These devices collect the sample in a storage chamber that may be sealed leaving zero headspace. Acceptable examples include Encore samplers or other coring devices. The samples are then chilled to 4°C and shipped to the laboratory for receipt within 48-hours of collection.

9.3.2 Method 5030: All soil samples received for analysis in according to Method 5030 are unpreserved. The sample is collected in container with minimal headspace and unopened until analysis. Acceptable examples include glass jars with Teflon lined lids. The samples are then chilled to 4°C and shipped to the laboratory. These samples have a maximum hold time of 14-days from collection.

10.0 QUALITY CONTROL

10.1 An *Initial Demonstration of Capability* study must be performed prior to the initial analysis for each analyst and whenever substantial change has occurred in the procedure or instrument. Refer to the Capability and Detection Limit Studies SOP for details.

10.2 A *Method Detection Limit* study must be performed for each new procedure, annually thereafter, and whenever a change in instrument occurs. Refer to the Capability and Detection Limit Studies SOP for details.

10.3 A *BFB Tune Check* must be performed at the beginning of each 12-hour sequence. A 1-ul (50-ng) injection of the working tune solution (which contains 4-Bromofluorobenzene) must meet the following ion abundance criteria. If the criteria are not met, reanalyze. An acceptable tune must be obtained before samples can be analyzed.

BFB (4-BROMOFLUOROBENZENE)
KEY IONS and ION ABUNDANCE CRITERIA
METHODS 624 / 8260B

Mass	Ion Abundance Criteria
50	15 – 40% of mass 95
75	30 – 60 % of mass 95
95	Base peak, 100% relative abundance
96	5 – 9 % of mass 95
173	< 2 % of mass 174
174	> 50 % of mass 95
175	5 – 9 % of mass 174
176	> 95 but < 101 % of mass 174
177	5 – 9 % of mass 176

10.4 *Internal Standards* (I.S.) must be added to all standards, QC samples and environmental samples.

10.4.1 Acceptance criteria for CCV standards are RT ± 30 seconds from that in the midpoint level standard of the most recent initial calibration (ICAL) and area counts within the range of -50 to +100% of those in the same (concentration level) linearity standard. These criteria are evaluated by the data system and printed on the Continuing Calibration Report. Failures in the CCV are automatically flagged on this report.

10.4.1.1 If the acceptance criteria are not met for the CCV, perform instrument maintenance then reanalyze the CCV or perform a new initial calibration.

10.4.2 There are no absolute acceptance criteria requirements for samples. The RT and Area for samples should be compared to that of the CCV for that day and assessed against the criteria for the CCV (i.e. RT $\pm$ 30 seconds and area counts within the range of -50 to +100%). These data are used as guidance in evaluating the response for samples.

10.4.2.1 If the acceptance criteria are not met for a sample, evaluate the chromatogram for obvious matrix effects/interferences. If interferences are evident, the sample should be diluted and reanalyzed. If the internal standard response for the sample is below 25% the analyst should consult with the Unit Supervisor and use discretion on whether to report, dilute and reanalyze, or re-extract and analyze the sample. This discretion is dependent on the experience of the analyst and their Supervisor and factors such as a consistent response for the I.S. should be considered. If reanalysis yields poor internal standard response, or if reanalysis is performed beyond the hold time, both sets of data should be reported to the client and a Case Narrative written.

10.4.2.2 For samples having a known matrix effect it is allowable to forego reanalysis due to "failing" I.S. response. These data, however, must be reported to the client with a Case Narrative informing them of the suspect data.

10.5 *Surrogate* (SURR) compounds must be added to all quality control samples, blanks, and samples.

10.5.1 Acceptance criteria are listed in the appropriate test code in LIMS.

10.5.2 Surrogate standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.

10.5.3 The reporting of data associated with failing surrogate standards must be documented with a CAR form.

10.5.4 If the acceptance criteria are not met, reanalyze the sample. If insufficient sample is available for reanalysis, report the original result with a Case Narrative to the client. If reanalysis fails to meet the acceptance criteria the original results should be reported with a Case Narrative to the client. If reanalysis does meet the acceptance criteria but was performed beyond the maximum hold time both sets of results should be reported to the client with an appropriate Case Narrative.

10.6 An *Initial Calibration Verification* (ICV) standard must be analyzed immediately after the initial linearity (ICAL). This is the analysis of a second source standard.

10.6.1 Acceptance criteria are listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the

acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier.

10.6.2 ICV standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.

10.6.3 The reporting of data associated with a failed ICV must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.6.4 Samples associated with an ICV that fails with a positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.7 A *Continuing Calibration Verification* (CCV) standard is a calibration source standard and must be analyzed at the beginning of each analytical sequence following an acceptable instrument tune. The 12-hour analytical sequence begins with the injection of BFB, continues through the analysis of the CCV, samples and QC samples.

10.7.1 Acceptance criteria for Method 8260B are the RF criteria (see below) for SPCCs and a RF for CCCs $\leq$ 20% difference from the initial calibration. Method 624 does not require the analysis of a CCV standard but, rather, evaluates the continuing integrity of the calibration using the laboratory control sample. If acceptable criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, recalibrate.

SPCC Criteria
$\geq$ 0.300 for Chlorobenzene and 1,1,2,2-Tetrachloroethane
$\geq$0.100 for Chloromethane, and 1,1-Dichloroethane, and Bromoform

CCC Compounds
1,1-Dichloroethene, 1,2-Dichloropropane, Chloroform, Ethylbenzene, Toluene and Vinyl chloride

10.7.2 The reporting of data associated with a failed CCV must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.7.3 Samples associated with a CCV that fails with a positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.8 A *Method Blank* (MBLK) must be prepared and analyzed at the beginning of each analytical sequence, batch of maximum 20 samples, or at a minimum of one per day, whichever is more frequent.

10.8.1 The acceptance criteria are < PQL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, re-extract and analyze the associated samples (alternatively, report data with an appropriate qualifier). Samples for compliance with our Wisconsin DNR certification must be evaluated down to the current MDL and corrective action taken if the blank exceeds the routine PQL.

10.8.2 MBLKs that fail to meet the acceptance criteria cause the sample results to be automatically flagged in LIMS with a "B" qualifier. MBLKs that are below the reporting limit but above the MDL are flagged in LIMS with a "b" qualifier. "b" flagged data is considered as meeting the acceptance criteria.

10.8.3 The reporting of data associated with a failed control sample must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.8.4 Samples associated with a MBLK that fails with positive bias can be reported without narration if the sample concentration is < PQL or greater than 10 times the blank contamination.

10.9 A *Laboratory Control Sample* is a second source standard that must be prepared and analyzed at the beginning of each analytical sequence, batch of maximum 20 samples, or at a minimum of one per day, whichever is more frequent. This standard serves as the daily calibration check for EPA Method 624.

10.9.1 Acceptance criteria are listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, re-extract and analyze the associated samples (alternatively, report data with an appropriate qualifier).

10.9.2 If insufficient sample is available for reanalysis the original result should be reported with a Case Narrative notifying the client of the quality control failure. If the hold time has expired and an acceptable re-analysis performed, both sets of data should be reported and the appropriate result flagged with a "H" qualifier as defined in the LIMS.

10.9.3 LCSs that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.

10.9.4 The reporting of data associated with a failed LCS must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.9.5 Samples associated with a LCS that fails with positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.10 A *Matrix Spike and Matrix Spike Duplicate* sample must be prepared and analyzed with each batch of maximum 20 samples per matrix and at a minimum of one per day.

10.10.1 Acceptance criteria are listed in the appropriate test code in LIMS. (Note: the accuracy criteria have been met provided at least either the MS or MSD meet the %R criteria.) If the accuracy criteria are not met in the MS or MSD, and the LCS is in control, assume matrix interference and report the results with an appropriate Case Narrative. If the precision criteria are not met, report the results with an appropriate Case Narrative.

10.10.2 MS/MSD's that fail to meet the accuracy criteria are automatically flagged in LIMS with a "S" qualifier. MSD's that fail to meet the precision criteria are automatically flagged in LIMS with a "R" qualifier.

10.10.3 The reporting of data associated with a failed MS/MSD must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.10.4 Samples associated with a MS/MSD that fails the accuracy criteria with positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.10.5 If the concentration measured in the sample is greater than 4-times the concentration of the spike, the spike amount used is insufficient and the MS/MSD not applicable.

10.10.6 The list of spiked compounds is the same as that for the LCS.

11.0 CALIBRATION AND STANDARDIZATION

Calibration data is documented and retained using the printouts from the instrument software and the ICAL Review Checklist (copy attached). Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

11.1 Perform the required preventive maintenance. Documentation is maintained in the PM Logbook for each instrument.

11.2 A new Initial Calibration (linearity; ICAL) is required as listed below. The concentration of the low standard must be set at or below the PQL for each compound.

- CCV failure that is uncorrectable through appropriate instrument maintenance
- New column
- Change electron multiplier

11.3 Instrument conditions and method settings are listed in section 18.0.

11.4 Purging and transfer to the Concentrator is initiated through the Solatek autosampler or the Tekmar 2016 ALS. The GC/MS is enabled by using the Method – Run pulldown menus on the instrument top window on the computer. When using the Solatek, the internal standards and surrogates are automatically added to each standard/sample. When using the Tekmar 2016, these are manually added to each analysis by adding 5.0-ul of the Working I.S./SURR Solution to the 5.0-ml of sample in the syringe.

11.5 Set up a sequence in the Sample Table Log in *Sequence* of the main menu. Enter the sequence as it is to be run, including the applicable analysis method. A calibration sequence must start with a BFB tune followed by the calibration standards then an ICV standard.

11.6 Click on *Position and Run*.

11.7 Generate the corresponding Quantitation Reports, BFB "Tune" Report and Response Factor Report.

11.7.1 The software calculates RF values for each standard as well as the average RF of all analytes.

11.7.2 On the BFB Report, evaluate the Pass/Fail column. An acceptable tune will Pass each of the criteria. Calibration can not continue with a failed tune. Details of Tune evaluation include:

- All spectra must be background-corrected using a single scan acquired no more than 20 scans prior to the beginning of the BFB peak. Do not subtract part of the BFB peak.
- Initial evaluation should use the auto-evaluate feature of the software. This feature evaluates the apex of the peak as well as the scans immediately on either side of the apex and automatically background corrects using a single scan no more than 20 scans prior to the beginning of the peak.
- If the auto-evaluation fails, select a different single spectrum or the average of several spectra. If these approaches fail, add additional spectra and re-evaluate. Guidance for these options is in the Environmental Data Analysis User's Guide for the Enviroquant software.
- Appropriate corrective action (e.g. instrument maintenance, new standard, re-calibration, etc) must be performed if an instrument continues to fail the tune criteria.

11.7.3 On the Response Factor Report, circle the %RSD values of each CCC and place a check mark next to the average RF of each SPCC.

11.8 The acceptance criteria for an acceptable ICAL are as follows:

11.8.1 For Method 8260B

- Minimum of 5 levels
- Average RF for the SPCCs must meet the following:
  - ≥0.300 for Chlorobenzene and 1,1,2,2-Tetrachloroethane
  - ≥0.100 for Chloromethane, and 1,1-Dichloroethane, and Bromoform
- %RSD for the CCCs must be < 30%
- Where these criteria are met and the %RSD of all individual compounds is ≤15, the calibration is considered linear and the average RF is used for concentration calculations
- If the %RSD > 15, averaging may be used to identify a linear curve. This technique assesses the average %RSD of all compounds in the calibration curve. If the RSD of all (target and non-target) compounds is ≤ 15%, the calibration can be considered acceptable and the average RF used. When used, the fact of its use and average RSD must be reported to the data user.

11.8.2 For Method 624

- Minimum of 3 levels
- average RF for each compound must have %RSD < 35
- Where these criteria are met, the calibration is considered linear and the average RF is used for concentration calculations.

11.9 If the linearity requirements are not met, take appropriate corrective actions and recalibrate. If the acceptance criteria are met, rename the method "WTRmmdd" or "SOILmmdd", (or similar) where mmdd designates the month and date of the new linearity.

11.9.1 Dropping levels from the calibration curve is allowable under the following conditions.

- Points may not be dropped solely to meet the acceptance criteria. There must be a justifiable reason for excluding a given standard.
- Individual analytes may be eliminated from the low or high points.
- Dropping a mid-level standard requires that all analytes be eliminated from that level.
- The required minimum number of calibrated levels remains (5 levels for 8260B, 3 levels for 624).
- If the low-level standard is removed from the curve, the PQL must be adjusted accordingly.

11.10 Analyze an ICV standard. The acceptance criteria must be met before continuing with sample analysis. Analysis of environmental samples cannot proceed without the generation of an acceptable linearity and an acceptable initial verification.

12.0 PROCEDURE

Preparation data is documented and retained using the printouts from the Injection Log and the VOA Soil Preparation Log (copy attached). This data must be maintained in

accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

12.1 SAMPLE PREPARATION – Water Samples Using the Solatek Autosampler

12.1.1 Load the VOA vials onto the autosampler. The purge and trap unit removes a 5-ml aliquot of sample and adds 5ul of the internal standard/surrogate solution for analysis. Dilutions up to 1:10 can be programmed and prepared by the autosampler. Higher dilutions, if necessary, must be prepared in volumetric flasks and transferred to VOA vials for analysis.

12.2 SAMPLE PREPARATION – Soil Samples Using the Solatek Autosampler

12.2.1 For **low-level samples collected directly into VOA vials** - Load the VOA vials onto the autosampler. The vials contain a stir bar and 5g of sample and the $NaHSO_4$ preservative (if used). The purge and trap unit adds 5ul of the internal standard/surrogate solution and 15-ml lab pure water for analysis.

12.2.2 For **low-level samples collected with coring devices** – Upon receipt in the lab, allow the unopened storage device to reach ambient temperature, extrude the sample into a tarred VOA vial containing a stir bar and record the sample weight. Record the weight in the logbook and place the vial on the autosampler. The purge and trap unit adds 5ul of the internal standard/surrogate solution and 15-ml lab pure water for analysis.

12.2.3 For **medium/high level samples collected with methanol preservation** – Transfer 1-ml of the extract to a 50-ml volumetric flask partially filled with lab pure water. (If the sample is expected to be very high in concentration use a lesser sample volume than 1-ml as the maximum sample:water ratio is 100-ul sample per 5.0-ml water.) Dilute the sample to the mark with lab pure water, transfer the solution to a VOA vial and load the vial onto the autosampler. Analyze the sample as a water sample (i.e. non-heated purge). The purge and trap unit adds 5ul of the internal standard/surrogate solution for analysis.

12.3 SAMPLE PREPARATION – Water Samples Using the Tekmar 2016 ALS

12.3.1 Remove 5.0-ml of sample from the VOA vial using a gas-tight syringe. If dilutions are necessary, use lesser sample diluted to a final volume of 5.0-ml in the syringe.

12.3.2 Add 5-ul of the Working I.S./SURR Solution to the syringe.

12.3.3 Using the sample valve on the ALS, transfer the sample into a 25-ml autosampler tube.

12.4 SAMPLE PREPARATION – Soil Samples Using the Tekmar 2016 ALS

12.4.1 For **low-level samples** – Using the top loading balance, transfer 5g of sample into a tarred autosampler tube and connect the tube onto the ALS. If the concentrations are expected to be high, use 1g or 0.5g of sample.

12.4.2 Add 5.0-ml of lab pure water in a gas-tight syringe then add 5.0-ul of the Working I.S./SURR Solution to the syringe.

12.4.3 Using the sample valve on the ALS, transfer the water/I.S./SURR into the autosampler tube.

12.4.4 For **medium/high level samples** – Using a top loading balance, transfer 5g of sample into a tarred VOA vial.

12.4.5 Using a disposable glass pipette, add 5-ml methanol then cap and shake the vial for 2-minutes.

12.4.6 Transfer approximately 2-ml of the extract into a vial for storage/retain. This extract may be stored in the dark at 4°C until analysis.

12.4.7 Add 5.0-ml of lab pure water in a gas-tight syringe then add 5.0-ul of the Working I.S./SURR Solution and 100-ul of the extract to the syringe. (Note: no more than 200-ul of methanol extract should be used for analysis.)

12.4.8 Using the sample valve on the ALS, transfer the sample into the autosampler tube.

12.5 ANALYSIS

Analytical data is documented and retained using the printouts from the instrument software. Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

12.5.1 Perform the required preventive maintenance. Documentation is maintained in the PM Logbook for each instrument.

12.5.2 When using the Solatek, the internal standards and surrogates are automatically added to each standard/sample. When using the Tekmar 2016, these are manually added to each analysis by adding 5.0-ul of the Working I.S./SURR Solution to the 5.0-ml of sample in the syringe.

12.5.3 The ICAL must be verified each "analytical sequence" prior to sample analysis by analyzing a calibration standard (CCV) at/near the mid-point of the curve (typically 50 ug/l). See the Quality Control section for the acceptance criteria. The 12-hour analytical sequence begins with the injection of BFB, continues through the analysis of the CCV, environmental samples and QC samples.

12.5.4 Set up a sequence in the Sample Table Log under *Sequence* of the main menu. Enter the sequence as it is to be run, including the applicable analysis method.

12.5.5 Click on *Position and Run*.

12.5.6 After each sample has run, evaluate the chromatogram and quantitate against the current initial linearity (ICAL).

12.5.7 Generate the corresponding Quantitation Reports, BFB "Tune" Report and Evaluate Continuing Calibration Report.

12.5.7.1 On the BFB Report, evaluate the Pass/Fail column. An acceptable tune will Pass each of the criteria. Analysis can not continue with a failed tune.

12.5.7.2 On the Evaluate Continuing Calibration Report, circle the %Dev values of each CCC as well as the Area of each internal standard, and place a check mark next to the CCRF of each SPCC.

12.5.8 Analysis of environmental samples cannot proceed without an acceptable continuing verification.

12.5.9 If the concentration of any target compound in a sample exceeds the initial calibration range, a new aliquot must be diluted and analyzed.

13.0 CALCULATIONS AND DATA HANDLING

Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

13.1 The HP software will print out all target analytes detected at a concentration at or above the MDL. The analyst must verify every target detected by evaluating the retention time and fit against the applicable CCV standard. These evaluations are accomplished by evaluating the characteristic ions through QEDIT as well as comparing the reference spectra. The Qvalue should be considered, however, the individual spectra must be evaluated in order to confidently identify a given analyte.

13.1.1 The data system software evaluates the retention time of each peak as well as a comparison of the characteristic ions to identify the compounds present. The characteristic ions of the reference spectrum are the three ions of greatest intensity (or any ions having a relative intensity greater than 30% if less than three ions are present). The following criteria are used for qualitative identification. An analyte may be confirmed as a proper identification only if these criteria are met.

- The characteristic ions of a compound must have a relative retention time of ± 0.06 minutes of the standard (RT ± 30 sec for Method 624).
- The relative intensities of the characteristic ions are within 20% of those ions in the reference spectrum (30% for Method 8260B). Example: for an ion having an abundance of 50% in the reference spectrum, the corresponding abundance

in a sample can range from 30% to 70% (Method 624) or 20% to 80% (Method 8260B) as appropriate.

- Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different retention times, otherwise, the isomers having a resolution of < 25% are identified as isomeric pairs.

13.1.2 Minimum levels for each analyte are established in the software at a concentration equivalent to the current on-column MDL value.

13.1.3 Manual peak integration's as well as the addition/deletion of analytes must be documented on the Quantitation Report. See the Manual Integration of Chromatographic Peaks SOP for details.

13.2 Response factors (RF) are calculated as follows:

$$RF = (A_x)(C_{IS}) / (A_{IS})(C_x)$$

Where: A_x = Area of characteristic ion for compound being measured
A_{IS} = Area of characteristic ion for compound being measured
C_{IS} = Concentration of the specific internal standard
C_x = Concentration of the compound being measured

13.3 The software calculates the sample concentration as follows:

INTERNAL STANDARD CALIBRATION

$$\text{Conc.} = \frac{(A_x)(I_s)(V_t)(DF)}{(A_{IS})(RF)(V_o)(V_i)}$$

Where: A_x = Area of characteristic ion for compound being measured
I_s = Amount of internal standard injected (ng)
V_t = Volume of total extract, taking into account dilution
A_{IS} = Area of characteristic ion for the internal standard
RF = Initial average response factor for compound being measured
V_o = Volume of water extracted (L), or mass of soil extracted (kg)
V_i = Volume of extract injected (ul)
DF = dilution factor

Integration for "gasoline" requires manual integration. Integration must include the sum of all ions eluting between the first and last peaks observed in the CCV or calibration standard, as appropriate. The sum of these peaks is reported as "Gasoline Range Organics". If the pattern of these peaks matches that of the standard, the sum of the peaks shall be reported as "Gasoline".

$$\text{Conc., ppb} = \frac{(A_x)\,(C_{std})\,(DF)}{(A_{std})(V_o)}$$

Where: A_x = Total ion area of sample
C_{std} = Concentration of standard injected (ng)
DF = dilution factor
A_{std} = Total ion area of standard
V_o = Volume of water purged (ml) or mass of soil purged (g)
NOTE: $(A_x)(C_{std}) / (A_{std})(RF)$ is calculated by the computer.

13.4 After review, enter final results into the LIMS system. Results flagged by the LIMS with an "E" qualifier are above the linear range of the instrument. There is less certainty in these data and, if sufficient extract and holding time are available, should be reanalyzed at an appropriate dilution. Details on the procedure for entering analytical data are in the Data Entry SOP.

13.5 The LIMS calculates the dry-weight concentration for solid samples as follows:

$$\text{Conc. Dry} = \frac{\text{(wet weight conc.)}}{(100 - \%\ \text{Moisture})}$$

14.0 METHOD PERFORMANCE

14.1 Initial Demonstration of Capability study data, Method Detection Limit study data and Performance Testing study data are maintained and available from the QA office.

15.0 POLLUTION PREVENTION

15.1 The quantity of chemicals purchased should be based on expected usage during their shelf life and the disposal cost of unused material.

15.2 Prepare the minimum amount of reagent and standard necessary.

16.0 WASTE MANAGEMENT

16.1 Refer to the Sample Disposal SOP for guidance on the disposal of any resulting residue, digestate, distillate, extract or standard.

17.0 REFERENCES

17.1 USEPA Method 624

17.2 SW-846 Method 5030B

17.3 SW-846 Method 5035

17.4 SW-846 Method 8260B

17.5 Indiana Dept of Environmental Management Non-rule Policy Document for Indiana Modified Method 5035, adopted April 20, 2000

17.6 Environmental Data Analysis User's Guide, HP G1032C Enviroquant Target Compound Software, 1992

17.7 Microbac Laboratories Quality Assurance Plan, current revision, all sections

18.0 TABLES, FORMS, CHECKLISTS, AND OTHER ATTACHMENTS

Non-gases Calibration Standard analyte list (1 page)
VOA Soil Preparation Log (1 page)
ICAL Review Checklist (1 page)
Instrument Conditions and Method Settings (3 pages)

Calibration Standard Compounds	
Non-gases Accustandard M-502A-R2-10X	Benzene; Bromobenzene; cis-1,3-Dichloropropene; Bromodichloromethane; Bromoform; n-Butylbenzene; sec-Butylbenzene; tert-Butylbenzene; Carbon tetrachloride; Chlorobenzene; Chloroform; 2-Chlorotoluene; 4-Chlorotoluene; Dibromochloromethane; 1,2-Dibromoethane; Dibromomethane; 1,2-Dibromo-3-chloropropane; 1,2-Dichlorobenzene; 1,3-Dichlorobenzene; 1,4-Dichlorobenzene; 1,1-Dichloroethane; 1,2-Dichloroethane; 1,1-Dichloroethene; cis-1,2-Dichloroethene; ; trans-1,2-Dichloroethene; 1,2-Dichloropropane; 1,3-Dichloropropane; 2,2-Dichloropropane; 1,1-Dichloropropene; trans-1,3-Dichloropropene; Ethylbenzene; Hexachlorobutadiene; Isopropylbenzene; p-Isopropyltoluene; Methylene chloride; Naphthalene; n-Propylbenzene; Styrene; 1,1,1,2-Tetrachloroethane; 1,1,2,2-Tetrachloroethane; Tetrachloroethene; Toluene; 1,1,1-Trichloroethane; 1,1,2-Trichloroethane; Trichloroethene; 1,2,3-Trichlorobenzene; 1,2,4-Trichlorobenzene; 1,2,3-Trichloropropane; 1,2,4-Trimethylbenzene; 1,3,5-Trimethylbenzene; o-Xylene; m-Xylene; p-Xylene

ICV/LCS/MS/MSD (2nd source verification) Standard Compounds	
Non-gases Supelco 502111	Benzene; Bromobenzene; cis-1,3-Dichloropropene; Bromodichloromethane; Bromoform; n-Butylbenzene; sec-Butylbenzene; tert-Butylbenzene; Carbon tetrachloride; Chlorobenzene; Chloroform; 2-Chlorotoluene; 4-Chlorotoluene; Dibromochloromethane; 1,2-Dibromoethane; Dibromomethane; 1,2-Dibromo-3-chloropropane; 1,2-Dichlorobenzene; 1,3-Dichlorobenzene; 1,4-Dichlorobenzene; 1,1-Dichloroethane; 1,2-Dichloroethane; 1,1-Dichloroethene; cis-1,2-Dichloroethene; ; trans-1,2-Dichloroethene; 1,2-Dichloropropane; 1,3-Dichloropropane; 2,2-Dichloropropane; 1,1-Dichloropropene; trans-1,3-Dichloropropene; Ethylbenzene; Isopropylbenzene; p-Isopropyltoluene; Methylene chloride; Naphthalene; n-Propylbenzene; Styrene; 1,1,1,2-Tetrachloroethane; 1,1,2,2-Tetrachloroethane; Tetrachloroethene; Toluene; 1,1,1-Trichloroethane; 1,1,2-Trichloroethane; Trichloroethene; 1,2,3-Trichlorobenzene; 1,2,4-Trichlorobenzene; 1,2,3-Trichloropropane; 1,2,4-Trimethylbenzene; 1,3,5-Trimethylbenzene; o-Xylene; m-Xylene; p-Xylene

Microbac Laboratories - Chicagoland Division

VOA Soil Preparation

Sample ID	Cont ID	Pres Type*	Initial Wt (g)	Final Wt (g)	Sample W (g)**	Ratio ***	Initials	Date & Time	Comments / Reagent ID

Version: _vc_1.0.1

* U (unpreserved), SB (sodium bisulfate)
M (methanol), E (Encore or similar)

** SAMP WT of pretared vials is adjusted for average 0.35g label weight
*** PFac = 5/SAMP WT

Microbac Laboratories
ICAL Review Checklist – VOA

Instrument ID: _____ Analyst:: _____

Linearity Date: _____ Quant. Method Name: _____

1st Level Technical Review

Review Element	Evaluation	Comments (use this space as needed)
SW-846 Method 8260B		
%RSD of CCCs <30 and circled?	[ ] Yes [ ] No [ ] NA	
Avg. RF of SPCCs meet method criteria and check-marked?	[ ] Yes [ ] No [ ] NA	
%RSD of all individual target components ≤15? OR Avg. %RSD of all (target and non-target) components ≤15?	[ ] Yes [ ] No [ ] NA [ ] Yes [ ] No [ ] NA	
Minimum of 5 calibration levels for all components?	[ ] Yes [ ] No [ ] NA	
EPA Method 624		
%RSD of each compound <35?	[ ] Yes [ ] No [ ] NA	
Minimum of 3 calibration levels for all components?	[ ] Yes [ ] No [ ] NA	
Miscellaneous		
Method properly calibrated and saved? (including)		
• RTs correct?	[ ] Yes [ ] No [ ] NA	
• Concentrations correct?	[ ] Yes [ ] No [ ] NA	
• Reference spectra updated?	[ ] Yes [ ] No [ ] NA	
• ICV acceptance criteria met?	[ ] Yes [ ] No [ ] NA	

Initials: _____ Date: _____

2nd Level Technical Review

Above assessment accurate [ ] Yes [ ] No
Data accurate in LIMS [ ] Yes [ ] No
If "No", list unacceptable evaluation(s): _____

LIMS QA Validation performed [ ] Yes [ ] No

Initials: _____ Date: _____

VOA CCCs	VOA SPCCs
1,1-Dichloroethene, 1,2-Dichloropropane, Chloroform, Ethylbenzene, Toluene, Vinyl chloride	*Criteria ≥ 0.300* Chlorobenzene, 1,1,2,2-Tetrachloroethane *Criteria ≥ 0.100* Chloromethane, 1,1-Dichloroethane, Bromoform

Instrument Conditions and Method Settings

Concentrator

Standby:	35°C
Purge:	11-minutes
Dry Purge:	6-minutes
Desorb preheat:	245°C
Desorb:	2-minutes at 250°C
Bake:	10-minutes at 260°C

Gas Chromatograph

Inlet:	240°C
Detector:	250°C

BFB-aq.m

Initial temperature:	35°C
Initial time:	2.0-minutes
Rate:	20°C / minute
Final temperature:	195°C
Final time:	0.0-minutes
Run time:	10.0-minutes

VOA-aq.m

Initial temperature:	35°C
Initial time:	2.0-minutes
Rate A:	8°C / minute
Final temperature:	130°C
Final time:	0.0-minutes
Rate B:	15°C / minute
Final temperature:	180°C
Final time:	0.0-minutes
Rate C:	25°C / minute
Final temperature:	230°C
Final time:	1.0-minutes
Run time:	20.21-minutes

Solatek Water Method				
Variable	Value		Variable	Value
Rinse Water Temp	90°C		Turbo Cool Temp	-20°C
Sample Cup Temp	30°C		GC Start	Start of Desorb
Sample Needle Temp	38°C		GC Cycle Time	0.00 min
Transfer Line Temp	150°C		Sample Heater	Off
Soil Valve Temp	100°C		Sample Temp	40°C
Sample Sweep Time	0.50 min		Sample Preheat Time	0.00 min
Needle Rinse Volume	7 mL		Purge Time	11.00 min
Needle Sweep Time	0.50 min		Dry Purge Time	6.00 min
Bake Rinse Volume	7 mL		Desorb Preheat Temp	245°C
Bake Sweep Time	0.50 min		Desorb Time	2.00 min
Bake Drain Time	0.50 min		Desorb Temp	250°C
Number of Bake Rinses	2		Bake Time	10.00 min
Valve Oven Temp	150°C		Bake Temp	260°C
Transfer Line Temp	150°C		Cryofocuser	Off
Sample Mount Temp	40°C		Standby Temp	100°C
MCS Temp	40°C		Focus Temp	-150°C
MCS Bake Time	310°C		Inject Time	1.00 min
Purge Ready Temp	35°C		Inject Temp	180°C
Purge Temp	0°C		Purge Temp	0°C

Solatek Soil Method				
Variable	Value		Variable	Value
Rinse Water Temp	90°C		MCS Bake Temp	310°C
Sample Cup Temp	40°C		Purge Ready Temp	37°C
Sample Needle Temp	60°C		Purge Temp	0°C
Transfer Line Temp	150°C		Turbo Cool Temp	-20°C
Soil Valve Temp	100°C		GC Start	Start of Desorb
Sample Sweep Time	0.50 min		GC Cycle Time	0.00 min
Needle Rinse Volume	7 mL		Dry Purge Time	6.00 min
Needle Sweep Time	0.75 min		Desorb Preheat Temp	245°C
Sample Preheat Time	0.00 min		Desorb Time	2.00 min
Preheat Stir	Off		Desorb Temp	250°C
Preheat Stir Mode	Spin		Bake Time	10.00 min
Preheat Stir Speed	1		Bake Temp	260°C
Purge Time	11.00 min		Cryofocuser	Off
Purge Stir	On		Standby Temp	100°C
Purge Stir Mode	Spin		Focus Temp	-150°C
Purge Stir Speed	5		Inject Time	1.00 min
Valve Oven Temp	150°C		Inject Temp	180°C
Transfer Line Temp	150°C		Sample Heater	Off
Sample Mount Temp	40°C		Sample Temp	40°C
MCS Temp	40°C		Purge Temp	0°C

Method Settings: Tekmar P&T 2000/3000/ALS2016				
Method Type	20XX			
MCS line temp	40		Purge temp	35
Purge rdy temp	35		Turbo cool temp	-20
Sample heater	Off		Desorb preheat	245
Prepurge time	0.0		Desorb time	2.0
Preheat time	0.0		Desorb temp	250
Sample temp	40		Sample drain	Off
Purge time	11.00		Bake time	10.0
Dry purge	6.0		Bake temp	260
GC start	Desstart		BGB off delay	2.0
Cryo focuser	Off		MCS Bake	250
GC cycle time	0.0		Line temp	120
Cryo standby	100		Valve temp	120
Cryo focus temp	-150		20XX line	120
Inj time	1.0		20XX valve	120
Cry inj temp	180			

STANDARD OPERATING PROCEDURE FOR SEMI-VOLATILE ORGANIC COMPOUNDS (SVOA) BY EPA METHOD 625 AND SW-846 METHOD 8270C

Originating Author: Nancy Tavitas
Revision Author: Nancy Tavitas, Brian Mills

This SOP is effective upon signed approval by the following:

Nancy T. Tavitas

Organics Manager — Date: 5/12/2006

Jeffrey M. Lorenz

QA/QC Manager — Date: 5/12/2006

DISCLAIMER: This SOP has been developed for use at the Microbac Laboratories, Merrillville, Indiana facility. It is intended for use by trained analysts. As written, this SOP may not be specifically applicable to the activities of other organizations.

Last Review Date:
No Changes Needed
Approved By:

1.0 TABLE OF CONTENTS

2.0 SCOPE AND APPLICATION

2.1 This is a GC/MS procedure for the determination of semi-volatile organic compounds. This procedure is applicable to the analysis of extracts from aqueous, non-aqueous liquid, and solid matrix samples. The applicable analytes, detection limits and routine reporting limits (PQL) are listed at the Limits tab of the applicable test codes in LIMS.

3.0 SUMMARY

3.1 Methods 8270C and 625 can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and are capable of being eluted, without derivitization, as sharp peaks from a gas chromatographic fused silica capillary column. Some of these compounds are: polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, nitrosamines, ethers, anilines, aromatic nitro compounds, and phenols.

3.2 Semi-volatile organic compounds are extracted from the sample matrix using methylene chloride. After concentration, the extract is injected into the GC/MS system and analyzed following the applicable criteria of SW-846 Method 8270C or EPA Method 625. Certain liquid sample matrices (e.g. oil) are miscible in methylene chloride and do not require the preliminary extraction but, rather, are diluted with the solvent and analyzed.

3.3 This procedure is based on the reference methods listed in section 17 of this document. This procedure contains the following listed deviations. These deviations are considered insignificant deviations from the reference methods.

3.3.1 EPA Method 625 requires the use of a packed GC column while our procedure uses a capillary column. This is considered insignificant as our procedure meets the acceptance criteria for an alternate column as defined in sections 13.1 and 8.2 of Method 625.

3.3.2 EPA Method 625 requires the separate and individual analysis of the base/neutral fraction and the acid fraction while our procedure uses a single analysis on the gas chromatograph. This is considered insignificant as our procedure meets the acceptance criteria for an alternate chromatographic conditions as defined in sections 13.1 and 8.2 of Method 625.

3.3.3 EPA Method 625 requires the spiking of all target analytes into the control samples while our procedure allows the rotating of spike analytes over a two-year basis. This rotating approach is consistent with the NELAC standards and is considered to provide sufficient data for evaluation and validation.

3.3.4 EPA Method 625 requires surrogate spike concentrations be at 100 ug/ml each. SW-846 Method 8270C suggests surrogate spike concentrations be at 100 ug/ml for the Base/Neutral compounds and 200 ug/ml for the Acid compounds. Our

procedure compromises on the concentrations as we spike at a level of 100 ug/ml for Base/Neutral compounds and 150 ug/ml for the Acid compounds.

4.0 DEFINITIONS

4.1 A list of definitions is in the Quality Assurance Plan. In addition to the terms defined in the QAP.

5.0 INTERFERENCES

5.1 Interferences are minimized through the use of ion counts and internal standards.

5.2 Contamination by carryover can occur when a low-level sample is analyzed after a high level sample. Solvent blanks should be analyzed in the instances to check for carryover effects.

6.0 SAFETY

6.1 Consult the current revision of the Chemical Hygiene Plan. Requirements for the use of personal protective equipment (e.g. safety glasses, lab coats, gloves) as well as other area-specific safety requirements (e.g. gas cylinders) and MSDS sheets are addressed in the CHP.

7.0 EQUIPMENT AND SUPPLIES

The following is a list of materials needed to perform the steps of this procedure as written. See the reference method(s) for equipment and supply specifications.

7.1 All volumetric glassware used shall be ASTM Class A. Glass microliter syringes are considered Class A provided they provided they come with a certificate attesting to the accuracy of the syringe. Syringes without vendor certification are considered Class B glassware. Class B glassware must be verified for accuracy on an annual basis and labeled with an appropriate correction.

7.2 GC/MS System consisting of the following:

7.2.1 OPTIONAL: HP 5890 Series II Gas Chromatograph with electronic pressure control (EPC)

7.2.2 HP 5971A or 5972 Mass Selective Detector

7.2.3 HP 7673 Autosampler/controller

7.2.4 Chromatographic column: Phenomenex ZB5-MS or equivalent; dimension specs length 30m, ID 0.32mm, film thickness 0.50 um or length 30m, ID 0.25mm, film thickness 0.25 um

7.2.5 OPTIONAL: HP 59822B Ion Gauge Controller

7.3 Computer with MS Chemstation software, monitor, and printer

7.4 Syringes: various sizes including 10-ul, 500-ul, and 1000-ul

7.5 Autosampler vials: 2-ml size with screw tops as well as 2-ml size with crimp tops

7.6 Crimper tool

7.7 400-ul glass inserts

8.0 REAGENTS AND STANDARDS

8.1 All reagents used must be analytical reagent (AR) grade or higher. All standards must be traceable to NIST, when available. Certificates of traceability must be obtained from the manufacturer. All reagents and standards must be documented in the appropriate preparation logbook. Refer to the requirements in the Labeling of Standards, Reagents, Digestates and Extracts SOP.

8.2 Reagents

All reagents are stored in the organics prep lab unless otherwise noted.

8.2.1 Methylene chloride, pesticide quality or greater

8.2.2 Methanol, pesticide quality or greater

8.3 Standards

All standards are stored in the Organics standard refrigerator unless otherwise instructed by the manufacturer's recommendation. Expiration of prepared standards must be performed in accordance with the Labeling of Standards, Reagents, Digestates and Extracts SOP.

8.3.1 Stock Tune Solution, 1000 ug/ml DFTPP, Benzidine, Pentachlorophenol, and 4,4'-DDT in methylene chloride: Accustandard Cat #M-625-TS-20X or equivalent.

8.3.2 Working Tune Solution, 50 ug/ml each: In a 10-ml volumetric flask, dilute to the mark 500-ul of the Stock Tune Solution with methylene chloride. Store the dilution into a screw top vial.

8.3.3 Stock Internal Standard (I.S.), 4000 ug/ml each in methylene chloride. Equivalent products from other vendors may be used.

VENDOR	CAT #	COMPOUNDS
Accustandard	Z-014J-PAK SVOA	1,4-dichlorobenzene-d4; naphthalene-d8; acenaphthalene-d10; phenanthrene-d10; chrysene-d12; perylene-d14

8.3.4 Stock Acid Surrogate Standard, 10000 ug/ml each in methanol. Equivalent products from other vendors may be used.

VENDOR	CAT #	COMPOUNDS
Supelco	4-7261	2-fluorophenol; phenol-d5; 2,4,6-tribromophenol

8.3.5 Stock Base/Neutral Surrogate Standard, 5000 ug/ml each in methanol. Equivalent products from other vendors may be used.

VENDOR	CAT #	COMPOUNDS
Supelco	4-7262	Nitrobenzene-d5; 2-fluorobiphenyl; terphenyl-d14

8.3.6 Stock Calibration Standards, 2000 ug/ml each in methylene chloride. Equivalent products from other vendors may be used.

MIX #	VENDOR	CAT #	COMPOUNDS
SVOA 1	Accustandard	M-8270-01	See Table in Section 18.0
SVOA 2	Accustandard	M-8270-02	
SVOA 3	Accustandard	M-8270-03	
SVOA 4A	Accustandard	M-8270-04A	
SVOA 4B	Accustandard	M-8270-04B	
SVOA 5	Accustandard	M-8270-05	
SVOA6	Accustandard	M-8270-06	
	Supelco / Protocol	4-8076 / S-730	Carbazole
	Supelco / Restek	4-8305-U / 30409	Pyridine

8.3.7 Intermediate Calibration Standards, 200 ug/ml each: In a 5-ml volumetric flask, dilute 500-ul of the Stock Calibration Standards, 100-ul of the Stock Acid Surrogate Standard, and 200-ul of the Stock Base/Neutral Surrogate Standard to volume with methylene chloride. Store dilutions in screw top vials.

8.3.8 Working Calibration Standards: In separate 1-ml volumetric flasks, prepare the following dilutions with methylene chloride. Transfer the dilutions into separate 1-ml screw top vials for storage. The I.S. concentration is 40 ug/ml.

Linearity Standard #	Vol. Inter Cal. Std, ul	Vol. Stock I.S., ul	Final Conc. ug/ml
1	50	10	10
2	100	10	20
3*	250	10	50
4	400	10	80
5	600	10	120
6	800	10	160

* typically used as the CCV

8.3.9 Stock Verification Standards, 2000 ug/ml each in methylene chloride. Equivalent products from other vendors may be used. When purchased from the same vendor as the calibration standards, the verification standards must be from a different lot number.

MIX #	VENDOR	CAT #	COMPOUNDS
SVOA 1	Accustandard	M-8270-01	See Table in Section 18.0
SVOA 2	Accustandard	M-8270-02	
SVOA 3	Accustandard	M-8270-03	
SVOA 4A	Accustandard	M-8270-04A	
SVOA 4B	Accustandard	M-8270-04B	
SVOA 5	Accustandard	M-8270-05	
SVOA6	Accustandard	M-8270-06	
	Supelco / Protocol	4-8076 / S-730	Carbazole
	Supelco / Restek	4-8305-U / 30409	Pyridine

8.3.10 Intermediate Verification Standards, 200 ug/ml each: In a 5-ml volumetric flask, dilute 500-ul of the Stock Calibration Standards, 100-ul of the Stock Acid Surrogate Standard, and 200-ul of the Stock Base/Neutral Surrogate Standard to volume with methylene chloride. Store dilutions in screw top vials.

8.3.11 Working ICV Standard, 50 ug/ml each: In a 1-ml volumetric flask, dilute 250-ul of the intermediate verification standards and 10-ul of the stock internal to the mark with methylene chloride. Transfer the dilution into a screw top vial. The final concentration of the each surrogate is 50 ug/ml and the concentration of each internal standard is 40 ug/ml.

8.3.12 LCS/MS/MSD: When prepared as detailed in the preparation SOPs, the final concentrations are 100 ug/l (3333 ug/kg) for all spiked analytes.

9.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

9.1 The client or other trained personnel collect samples. Samples received at the laboratory are considered representative unless otherwise noted.

9.2 Extracts are stored at <10°C in the Organics sample freezer located in the GC/SVOA lab.

9.3 Analysis must be performed within 40 days of extraction.

10.0 QUALITY CONTROL

10.1 An *Initial Demonstration of Capability* study must be performed prior to the initial analysis for each analyst and whenever substantial change has occurred in the procedure or instrument. Refer to the Capability and Detection Limit Studies SOP for details.

10.2 A *Method Detection Limit* study must be performed for each new procedure, annually thereafter, and whenever a change in instrument occurs. Refer to the Capability and Detection Limit Studies SOP for details.

10.3 A *DFTPP Tune Check* must be performed at the beginning of each 12-hour sequence. A 1-ul (50-ng) injection of the working tune solution (which contains DFTPP) must meet the following ion abundance criteria. If the criteria are not met, reanalyze. An acceptable tune must be obtained before samples can be analyzed.

DFTPP (DECAFLUOROTRIPHENYLPHOSPHINE)
KEY IONS and ION ABUNDANCE CRITERIA
METHODS 625 / 8270C

Mass	Ion Abundance Criteria
51	30 – 60% of mass 198
68	< 2% of mass 69
69	Present
70	< 2% of mass 69
127	40 – 60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5 – 9% of mass 198
275	10 – 30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17 – 23% of mass 442

10.4 The *Tailing Factors* must be evaluated at the beginning of each 12-hour sequence as needed. Evaluate the tailing for Benzidine on days which Benzidine is being analyzed. Evaluate the tailing for Pentachlorophenol on days which the Acids are being analyzed. A 1-ul injection of the working tune solution (which contains Benzidine and Pentachlorophenol) must yield a tailing factor less than 3.0 for Benzidine and less than 5 for Pentachlorophenol. The tailing factors are calculated (according to Figure 13 in Method 625) by the instrument software and documented on the instrument printout. If the tailing factor criterion cannot be achieved, perform instrument maintenance or re-prepare the tune solution, and reanalyze. Instrument maintenance may include cutting off the first 6-12 inches of the column. Tailing factor criteria must be met before samples can be analyzed.

10.5 *Internal Standards* (I.S.) must be added to all standards, QC samples and environmental samples.

10.5.1 Acceptance criteria for CCV standards are RT $\pm$ 30 seconds from that in the midpoint level standard of the most recent initial calibration (ICAL) and area counts within the range of -50 to +100% of those in the same

(concentration level) linearity standard. These criteria are evaluated by the data system and printed on the Continuing Calibration Report. Failures in the CCV are automatically flagged on this report.

10.5.1.1 If the acceptance criteria are not met for the CCV, perform instrument maintenance then reanalyze the CCV or perform a new initial calibration.

10.5.2 There are no absolute acceptance criteria requirements for samples. The RT and Area for samples should be compared to that of the CCV for that day and assessed against the criteria for the CCV (i.e. RT $\pm$ 30 seconds and area counts within the range of -50 to +100%). These data are used as guidance in evaluating the response for samples.

10.5.2.1 If the acceptance criteria are not met for a sample, evaluate the chromatogram for obvious matrix effects/interferences. If interferences are evident, the sample should be diluted and reanalyzed. If the internal standard response for the sample is below 25% the analyst should consult with the Unit Supervisor and use discretion on whether to report, dilute and reanalyze, or re-extract and analyze the sample. This discretion is dependent on the experience of the analyst and their Supervisor and factors such as a consistent response for the I.S. should be considered. If reanalysis yields poor internal standard response, or if reanalysis is performed beyond the hold time, both sets of data should be reported to the client and a Case Narrative written.

10.5.2.2 For samples having a known matrix effect (e.g. extracts from MGP sites) it is allowable to forego reanalysis due to "failing" I.S. response. These data, however, must be reported to the client with a Case Narrative informing them of the suspect data.

10.6 *Surrogate* (SURR) compounds must be added to all quality control samples, blanks, and samples.

10.6.1 Acceptance criteria are listed in the appropriate test code in LIMS. One acid and one Base/Neutral surrogate may be outside of the acceptance criteria.

10.6.2 Surrogate standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.

10.6.3 The reporting of data associated with failing surrogate standards must be documented with a CAR form.

10.6.4 If the acceptance criteria are not met, reprepare, reanalyze, or re-extract and analyze the sample as appropriate. If insufficient sample is available for re-extraction, report the original result with a Case Narrative to the client. If reanalysis fails to meet the acceptance criteria the original results

should be reported with a Case Narrative to the client. If reanalysis does meet the acceptance criteria but the re-extraction was performed beyond the maximum hold time both sets of results should be reported to the client with an appropriate Case Narrative.

10.7 An *Initial Calibration Verification* (ICV) standard must be analyzed immediately after the initial linearity (ICAL). This is the analysis of a second source standard.

10.7.1 Acceptance criteria are listed in the appropriate test code in LIMS. If the acceptance criteria are not met, evaluate the recoveries against the nominal window of ±30 %R. If this criterion are met the analysis of the ICV is acceptable. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier.

10.7.2 ICV standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.

10.7.3 The reporting of data associated with a failed ICV must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.7.4 Samples associated with an ICV that fails with a positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.8 A *Continuing Calibration Verification* (CCV) standard is a calibration source standard and must be analyzed at the beginning of each analytical sequence following an acceptable instrument tune. The 12-hour analytical sequence begins with the injection of DFTPP, continues through the analysis of the CCV, samples and QC samples.

10.8.1 Acceptance criteria for Method 8270 are RF for SPCCs ≥ 0.050 and RF for CCCs ≤ 20% difference from the initial calibration. (SPCCs and CCCs are listed in the table below.) Acceptance criteria for Method 625 are responses ≤ 20% difference from the initial calibration for any target analyte. If acceptable criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, recalibrate.

10.8.2 The reporting of data associated with a failed CCV must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.8.3 Samples associated with a CCV that fails with a positive bias can be reported without narration if the sample concentration is below the reporting limit.

SPCCs	
N-nitroso-di-n-propylamine	2,4-dinitrophenol
Hexachlorocyclopentadiene	4-nitrophenol

CCCs	
B/N Fraction	*Acid Fraction*
Acenaphthene	4-Chloro-3-methylphenol
1,4-dichlorobenzene	2,4-dichlorophenol
Hexachlorobutadiene	2-nitrophenol
Diphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

10.9 A *Method Blank* must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per day.

10.9.1 The acceptance criteria are < PQL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, re-extract and analyze the associated samples (alternatively, report data with an appropriate qualifier). Samples for compliance with our Wisconsin DNR certification must be evaluated down to the current MDL and corrective action taken if the blank exceeds the routine PQL.

10.9.2 MBLKs that fail to meet the acceptance criteria cause the sample results to be automatically flagged in LIMS with a "B" qualifier. MBLKs that are below the reporting limit but above the MDL are flagged in LIMS with a "b" qualifier. "b" flagged data is considered as meeting the acceptance criteria.

10.9.3 The reporting of data associated with a failed control sample must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.9.4 Samples associated with a MBLK that fails with positive bias can be reported without narration if the sample concentration is < PQL or greater than 10 times the blank contamination.

10.10 A *Laboratory Control Sample* must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per day.

10.10.1 Acceptance criteria are listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, re-extract and analyze the associated samples (alternatively, report data with an appropriate qualifier).

10.10.2 If insufficient sample is available for reanalysis the original result should be reported with a Case Narrative notifying the client of the

quality control failure. If the hold time has expired and an acceptable re-analysis performed, both sets of data should be reported and the appropriate result flagged with a "H" qualifier as defined in the LIMS.

10.10.3 LCSs that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.

10.10.4 The reporting of data associated with a failed LCS must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.10.5 Samples associated with a LCS that fails with positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.10.6 When prepared for samples being analyzed by Method 8270C, the spiked analytes consist of the compounds listed in section 5.5.1 of Method 3500B. When prepared for samples being analyzed by Method 625, the spike analytes consist of the compounds listed in section 5.5.1 of Method 3500B plus an additional 10-12 compounds listed in Table 6 of Method 625. These additional compounds are changed at approximate 6-month intervals so that all of the Table 6 compounds can be evaluated over a two-year period.

10.11 A *Matrix Spike and Matrix Spike Duplicate* sample must be prepared and analyzed with each batch of maximum 20 samples per matrix and at a minimum of one per day.

10.11.1 Acceptance criteria are listed in the appropriate test code in LIMS. (Note: the accuracy criteria have been met provided at least either the MS or MSD meet the %R criteria.) If the accuracy criteria are not met in the MS or MSD, and the LCS is in control, assume matrix interference and report the results with an appropriate Case Narrative. If the precision criteria are not met, report the results with an appropriate Case Narrative.

10.11.2 MS/MSD's that fail to meet the accuracy criteria are automatically flagged in LIMS with a "S" qualifier. MSD's that fail to meet the precision criteria are automatically flagged in LIMS with a "R" qualifier.

10.11.3 The reporting of data associated with a failed MS/MSD must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.11.4 Samples associated with a MS/MSD that fails the accuracy criteria with positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.11.5 If the concentration measured in the sample is greater than 4-times the concentration of the spike, the spike amount used is insufficient and the MS/MSD not applicable.

10.11.6 The list of spiked compounds is the same as that for the LCS.

11.0 CALIBRATION AND STANDARDIZATION

Calibration data is documented and retained using the printouts from the instrument software and the ICAL Review Checklist. Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

11.1 Perform the required preventive maintenance. Documentation is maintained in the PM Logbook for each instrument.

11.2 A new Initial Calibration (linearity; ICAL) is required as listed below. The concentration of the low standard must be set at or below the routine PQL for each compound.

- CCV failure that is uncorrectable through appropriate instrument maintenance (see section 10 for additional guidance)
- New column
- Change electron multiplier

11.3 Instrument conditions are as follows:

Zone Temperatures

Inlet:	On	Setpoint: 250°C
Detector:	On	Setpoint: 280°C

DFTPP.m

Injection size:	1-ul		
Initial Temp:	150°C		
Initial Time:	0.75-minute		
Rate A:	25°C / minute	Rate B:	12°C / minute
Final Temp:	320°C	Final Temp:	250°C
Final Time:	1.25-minutes	Final Time:	0.0-minutes
Run Time:	8.8-minutes		

8270-Aq.m

Injection size:	1-ul		
Initial Temp:	40°C		
Initial Time:	0.5-minute		
Rate A:	22°C / minute	Rate B:	35°C / minute
Final Temp:	220°C	Final Temp:	325°C
Final Time:	0-minutes	Final Time:	3-minutes
Run Time:	16-minutes		

11.4 Set up a sequence in the Sample Table Log under *Sequence* of the main menu. Enter the sequence as it is to be run, including the applicable analysis method. A calibration sequence must start with a DFTPP tune followed by the calibration standards then an ICV standard.

11.5 Click on *Position and Run*.

11.6 Generate the corresponding Quantitation Reports, DFTPP "Tune" Report and Response Factor Report.

11.6.1 The software calculates RF values for each standard as well as the average RF of all analytes.

11.6.2 On the DFTPP Report, evaluate the Pass/Fail column. An acceptable tune will Pass each of the criteria. Calibration can not continue with a failed tune. Details of Tune evaluation include:

- All spectra must be background-corrected using a single scan acquired no more than 20 scans prior to the beginning of the DFTPP peak. Do not subtract part of the DFTPP peak.
- Initial evaluation should use the auto-evaluate feature of the software. This feature evaluates the apex of the peak as well as the scans immediately on either side of the apex and automatically background corrects using a single scan no more than 20 scans prior to the beginning of the peak.
- If the auto-evaluation fails, select a different single spectrum or the average of several spectra. If these approaches fail, add additional spectra and re-evaluate. Guidance for these options is in the Environmental Data Analysis User's Guide for the Enviroquant software.
- Appropriate corrective action (e.g. instrument maintenance, new standard, re-calibration, etc) must be performed if an instrument continues to fail the tune criteria.

11.6.3 The Quantitation Report for Pentachlorophenol and Benzidine must show the Tailing factor for each. Calibration can not continue with failed tailing.

11.6.4 On the Response Factor Report, circle the %RSD values of each CCC and place a check mark next to the average RF of each SPCC.

11.7 The acceptance criteria for an acceptable ICAL are as follows:

11.7.1 For Method 8270C

- Minimum of 5 levels
- Average RF for the SPCCs must be $\geq$ 0.050
- %RSD for the CCCs must be < 30%
- Where these criteria are met and the %RSD of all individual compounds is $\leq$15, the calibration is considered linear and the average RF is used for concentration calculations
- If the %RSD > 15, averaging may be used to identify a linear curve. This technique assesses the average %RSD of all compounds in the calibration

curve. If the RSD of all (target and non-target) compounds is ≤ 15%, the calibration can be considered acceptable and the average RF used. When used, the fact of its use and average RSD must be reported to the data user.

11.7.2 For Method 625

- Minimum of 3 levels
- average RF for each compound must have %RSD < 35
- Where these criteria are met, the calibration is considered linear and the average RF is used for concentration calculations.

11.8 If the linearity requirements are not met, take appropriate corrective actions and recalibrate. If the acceptance criteria are met, rename the method "SVOAmmdd", (or similar) where mmdd designates the month and date of the new linearity.

11.8.1 Dropping levels from the calibration curve is allowable under the following conditions.

- Points may not be dropped solely to meet the acceptance criteria. There must be a justifiable reason for excluding a given standard.
- Individual analytes may be eliminated from the low or high points.
- Dropping a mid-level standard requires that all analytes be eliminated from that level.
- The required minimum number of calibrated levels remains (5 levels for 8270C, 3 levels for 625).
- If the low-level standard is removed from the curve, the PQL must be adjusted accordingly.

11.9 Analyze an ICV standard. The acceptance criteria must be met before continuing with sample analysis. Analysis of environmental samples cannot proceed without the generation of an acceptable linearity and an acceptable initial verification.

12.0 PROCEDURE

Analytical data is documented and retained using the printouts from the instrument software. Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

12.1 Perform the required preventive maintenance. Documentation is maintained in the PM Logbook for each instrument.

12.2 The ICAL must be verified each "analytical sequence" prior to sample analysis by analyzing a calibration standard (CCV) at/near the mid-point of the curve (typically 50 or 80 ug/ml). See the Quality Control section for the acceptance criteria. The 12-hour analytical sequence begins with the injection of DFTPP, continues through the analysis of the CCV, environmental samples and QC samples.

12.3 Set up a sequence in the Sample Table Log under *Sequence* of the main menu. Enter the sequence as it is to be run, including the applicable analysis method.

12.3.1 To prepare sample extracts for analysis, withdraw 200-ul of the extract with a syringe and place it into a 1.0-ml autosampler vial containing a glass insert. Add

2.0-ul of the stock internal standard. The concentration of the internal standards will be 40 ug/ml each. NOTE: All extracts, including dilutions, must be spiked with the internal standards at 40 ug/ml.

12.4 Click on *Position and Run*.

12.5 After each sample has run, evaluate the chromatogram and quantitate against the current initial linearity (ICAL).

12.6 Generate the corresponding Quantitation Reports, DFTPP "Tune" Report and Evaluate Continuing Calibration Report.

12.6.1 On the DFTPP Report, evaluate the Pass/Fail column. An acceptable tune will Pass each of the criteria. Analysis can not continue with a failed tune.

12.6.2 The Quantitation Report for Pentachlorophenol and Benzidine must show the Tailing factor for each. Calibration can not continue with failed tailing.

12.6.3 On the Evaluate Continuing Calibration Report, circle the %Dev values of each CCC as well as the Area of each internal standard, and place a check mark next to the CCRF of each SPCC.

12.7 Analysis of environmental samples cannot proceed without an acceptable continuing verification.

12.8 If the concentration of any target compound in a sample exceeds the initial calibration range, a new aliquot of that extract must be diluted and analyzed.

13.0 CALCULATIONS AND DATA HANDLING

Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

13.1 The HP software will print out all target analytes detected at a concentration at or above the MDL. The analyst must verify every target detected by evaluating the retention time and fit against the applicable CCV standard. These evaluations are accomplished by evaluating the characteristic ions through QEDIT as well as comparing the reference spectra. The Qvalue should be considered, however, the individual spectra must be evaluated in order to confidently identify a given analyte.

13.1.1 The data system software evaluates the retention time of each peak as well as a comparison of the characteristic ions to identify the compounds present. The characteristic ions of the reference spectrum are the three ions of greatest intensity (or any ions having a relative intensity greater than 30% if less than three ions are present). The following criteria are used for qualitative identification. An analyte may be confirmed as a proper identification only if these criteria are met.

- The characteristic ions of a compound must have a relative retention time of ± 0.06 minutes of the standard (RT ± 30 sec for Method 624).
- The relative intensities of the characteristic ions are within 20% of those ions in the reference spectrum (30% for Method 8260B). Example: for an ion having an abundance of 50% in the reference spectrum, the corresponding abundance in a sample can range from 30% to 70% (Method 624) or 20% to 80% (Method 8260B) as appropriate.
- Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different retention times, otherwise, the isomers having a resolution of < 25% are identified as isomeric pairs.

13.1.2 Minimum levels for each analyte are established in the software at a concentration equivalent to the current on-column MDL value.

13.1.3 Manual peak integration's as well as the addition/deletion of analytes must be documented on the Quantitation Report. See the Manual Integration of Chromatographic Peaks SOP for details.

13.2 Response factors (RF) are calculated as follows:

$$RF = (A_x)(C_{IS}) / (A_{IS})(C_x)$$

Where: A_x = Area of characteristic ion for compound being measured
A_{IS} = Area of characteristic ion for compound being measured
C_{IS} = Concentration of the specific internal standard
C_x = Concentration of the compound being measured

13.3 The software calculates the sample concentration as follows:

$$\text{Conc.} = \frac{(A_x)(I_s)(V_t)(DF)}{(A_{IS})(RF)(V_o)(V_i)}$$

Where: A_x = Area of characteristic ion for compound being measured
I_s = Amount of internal standard injected (ng)
V_t = Volume of total extract, taking into account dilution
A_{IS} = Area of characteristic ion for the internal standard
RF = Initial average response factor for compound being measured
V_o = Volume of water extracted (L), or mass of soil extracted (kg)
V_i = Volume of extract injected (ul)
DF = dilution factor

13.4 After review, enter final results into the LIMS system. Results flagged by the LIMS with an "E" qualifier are above the linear range of the instrument. There is less certainty in these data and, if sufficient extract and holding time are available, should be reanalyzed at an appropriate dilution. Details on the procedure for entering analytical data are in the Data Entry SOP.

13.5 The LIMS calculates the dry-weight concentration for solid samples as follows:

$$\text{Conc. Dry} = \frac{\text{(wet weight conc.)}}{\text{(100 - \% Moisture)}}$$

14.0 METHOD PERFORMANCE

14.1 Initial Demonstration of Capability study data, Method Detection Limit study data and Performance Testing study data are maintained and available from the QA office.

15.0 POLLUTION PREVENTION

15.1 The quantity of chemicals purchased should be based on expected usage during their shelf life and the disposal cost of unused material.

15.2 Prepare the minimum amount of reagent and standard necessary.

16.0 WASTE MANAGEMENT

16.1 Refer to the Sample Disposal SOP for guidance on the disposal of any resulting residue, digestate, distillate, extract or standard.

17.0 REFERENCES

17.1 USEPA Method 625

17.2 SW-846 Method 8270C

17.3 SOP Preparation of Aqueous Samples Using Liquid-Liquid Extraction by SW-846 Method 3510C, current revision.

17.4 SOP Preparation of Aqueous Samples Using Continuous Liquid-Liquid Extraction by SW-846 Method 3520C, current revision.

17.5 SOP Preparation of Non-Aqueous Samples Using Sonication by SW-846 Method 3550B, current revision.

17.6 Environmental Data Analysis User's Guide, HP G1032C Enviroquant Target Compound Software, 1992

17.7 Microbac Laboratories Quality Assurance Plan, current revision, all sections

18.0 TABLES, FORMS, CHECKLISTS, AND OTHER ATTACHMENTS

Table of ICAL & Verification Standard compounds (1 page)
ICAL Review Checklist (1 page)

Calibration Standard Compounds	
M-8270-01	Aniline Benzyl alcohol Bis(2-Chloroethyl)ether 1,2-Dichlorobenzene Bis(2-Chloroisopropyl)ether 2-Chlorophenol 1,3-Dichlorobenzene 1,4-Dichlorobenzene Hexachloroethane 2-Methylphenol 4-Methylphenol N-Nitrosodimethyamine N-Nitrosodi-n-propylamine Phenol
M-8270-02	Acetophenone Benzoic acid bis(2-Chloroethoxy)methane 4-Chloroaniline 4-Chloro-3-methylphenol 2,4-Dichlorophenol 2,6-Dichlorophenol 2,4-Dimethylphenol Hexachlorobutadiene Isophorone Naphthalene Nitrobenzene 2-Nitrophenol 1,2,4-Trichlorobenzene 2-Methylnaphthalene
M-8270-03	Acenaphthene Acenaphthylene 2-Chloronaphthalene 4-Chlorophenyl phenyl ether Dibenzofuran Diethyl phthalate 2,4-Dinitrophenol 2,4-Dinitrotoluene 2,6-Dinitrotoluene Fluorene Hexachlorocyclopentadiene 2-Nitroaniline 3-Nitroaniline 4-Nitroaniline 4-Nitrophenol 2,4,5-Trichlorophenol 2,4,6-Trichlorophenol Dimethylphthalate
M-8270-04A	Anthracene 4-Bromophenyl phenyl ether Di-n-butyl phthalate 4,6-Dinitro-2-methylphenol Fluoranthene Hexachlorobenzene Pentachlorophenol Phenanthrene
M-8270-04B	1,2-Diphenylhydrazine N-Nitrosodiphenylamine
M-8270-05	Benzidine Benzo(a)anthracene bis(2-Ethylhexyl) phthalate Butyl benzyl phthalate Chrysene 3,3'-Dichlorobenzidine Pyrene
M-8270-06	Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(g,h,i)perylene Benzo(a)pyrene Dibenz(a,h)anthracene Di-n-octyl phthalate Indeno(1,2,3-cd)pyrene
4-8076	Carbazole
4-8305-U	Pyridine

Microbac Laboratories
ICAL Review Checklist – SVOA

Instrument ID: _____ Analyst:: _____

Linearity Date: _____ Quant. Method Name: _____

1st Level Technical Review

Review Element	Evaluation	Comments (use this space as needed)
SW-846 Method 8270C		
%RSD of CCCs <30 and circled?	[ ] Yes [ ] No [ ] NA	
Avg. RF of SPCCs meet method criteria and check-marked?	[ ] Yes [ ] No [ ] NA	
%RSD of all individual target components ≤15?	[ ] Yes [ ] No [ ] NA	
OR		
Avg. %RSD of all (target and non-target) components ≤15?	[ ] Yes [ ] No [ ] NA	
Minimum of 5 calibration levels for all components?	[ ] Yes [ ] No [ ] NA	
EPA Method 625		
%RSD of each compound <35?	[ ] Yes [ ] No [ ] NA	
Minimum of 3 calibration levels for all components?	[ ] Yes [ ] No [ ] NA	
Miscellaneous		
Method properly calibrated and saved? (including)		
• RTs correct?	[ ] Yes [ ] No [ ] NA	
• Concentrations correct?	[ ] Yes [ ] No [ ] NA	
• Reference spectra updated?	[ ] Yes [ ] No [ ] NA	
• ICV acceptance criteria met?	[ ] Yes [ ] No [ ] NA	

Initials: _____ Date: _____

2nd Level Technical Review

Above assessment accurate [ ] Yes [ ] No
Data accurate in LIMS [ ] Yes [ ] No
If "No", list unacceptable evaluation(s): _____

LIMS QA Validation performed [ ] Yes [ ] No

Initials: _____ Date: _____

SVOA CCCs	SVOA SPCCs
Acenaphthene, 1,4-Dichlorobenzene, Hexachlorobutadiene, Diphenylamine, Di-n-octyl phthalate, Fluoranthene, Benzo(a)pyrene, 4-Chloro-3-methylphenol, 2,4-Dichlorophenol, 2-Nitrophenol, Phenol, Pentachlorophenol, 2,4,6-Trichlorophenol	*Criteria ≥ 0.050* N-Nitrosodi-n-propylamine, Hexachlorocyclopentadiene, 2,4-Dinitrophenol, 4-Nitrophenol

Revision 2, 5/5/06

STANDARD OPERATING PROCEDURE FOR SPECIFIC GRAVITY USING SM METHOD 2710F AND DENSITY USING A MODIFIED SM METHOD 2710F

Originating Author: Amanda Shebish
Revision Author:

This SOP is effective upon signed approval by the following:

Troy M Goehl — Inorganics Manager — 10-27-2005 — Date

Jeffrey M. Loeme — QA/QC Manager — 10.27.05 — Date

DISCLAIMER: This SOP has been developed for use at the Microbac Laboratories, Merrillville, Indiana facility. It is intended for use by trained analysts. As written, this SOP may not be specifically applicable to the activities of other organizations.

Last Review Date:
No Changes Needed
Approved By:

1.0 TABLE OF CONTENTS

2.0 SCOPE AND APPLICATION

2.1 This is a gravimetric procedure for the determination of Specific Gravity and Density. This procedure is applicable to the analysis of aqueous, non-aqueous liquid, drinking water, and solid matrix samples.

2.2 The routine reporting limit (PQL) for Specific Gravity (SG) is 0.01. Specific Gravity is a unitless analyte. Results are corrected for temperature to 4°C.

2.3 The routine reporting limit (PQL) for Density is 0.1 g/ml.

3.0 SUMMARY

3.1 Specific gravity (SG) is the ratio of masses of equal volumes of sample and distilled water. The SG is determined by comparing the mass of a known volume of sample to the mass of the same volume of water. Sample temperature is measured at the SG is corrected so match a standard of 4 degrees Celsius.

3.2 Density is the mass of a substance per unit of volume. Density is determined by weighing a "volume" of sample and measuring the mass associated with that volume.

3.3 This procedure is based on the reference methods listed in section 17 of this document. This procedure contains no significant deviation from the reference method for the determination of Specific Gravity. The determination of Density is made using a modified procedure of that used for SG.

4.0 DEFINITIONS

4.1 A list of definitions is in the Quality Assurance Plan. In addition to the terms defined in the QAP.

5.0 INTERFERENCES

5.1 None

6.0 SAFETY

6.1 Consult the current revision of the Chemical Hygiene Plan.

7.0 EQUIPMENT AND SUPPLIES

The following is a list of materials needed to perform the steps of this procedure as written. See the reference method(s) for equipment and supply specifications.

7.1 Analytical balance, Mettler AE-100 or equivalent

7.2 Plastic sample cups

7.3 Thermometer capable of measuring the temperature of the water and environmental samples

7.4 Volumetric pipette, class A, 10-ml

7.5 Pipette bulb

7.6 Graduated cylinder, various volumes

7.7 Wooden applicator stick, metal spatula or equivalent

8.0 REAGENTS AND STANDARDS

8.1 All reagents used must be analytical reagent (AR) grade or higher. All standards must be traceable to NIST, when available. Certificates of traceability must be obtained from the manufacturer. All reagents and standards must be documented in the appropriate preparation logbook. Refer to the requirements in the Labeling of Standards, Reagents, Digestates and Extracts SOP.

8.2 Reagents

8.2.1 Lab pure water: Analyte free water is prepared as described in the Quality Assurance Plan. Use the water from any of the DI taps located in the lab. Store this water in a plastic container marked as "Specific Gravity Water" (or similar) in the standards/reagent cooler in the main wet chemistry lab. Water must be in the range of 0.1-6°C prior to use.

8.2.2 Hydrochloric acid (HCl), concentrated: Obtain from the metals department.

8.2.3 1:1 (approximate) HCl: In a plastic container, mix equal volumes of concentrated HCl and DI water. Store this in the cabinets located in the main wet chemistry lab. Prepare as needed.

8.3 Standards

8.3.1 None.

9.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

9.1 The client or other trained personnel collect samples. Samples received at the laboratory are considered representative unless otherwise noted.

9.2 Samples should be collected in glass or plastic containers. Preservation consists of storage in the range of 0.1-6°C. Samples are stored in the coolers located in the

sample receipt area. Samples that fail to meet the preservation criteria are noted as such on the Cooler Inspection Report in the Login process.

9.3 No maximum allowable hold time is mandated for this analyte. An internally defined hold time of 28-days has been established.

10.0 QUALITY CONTROL

10.1 All Specific Gravity measurements are performed in duplicate. Obvious weight discrepancies between the two readings indicates sample matrix or procedural problems. If this occurs, repeat the analysis of the sample in order to identify an accurate and precise measurement.

10.2 A *Method Blank (MBLK)* must be analyzed with each batch of maximum 20 samples and at a minimum of one per day.

10.2.1 There are no acceptance criteria for the method blank. This sample is used solely to determine the reference gravity for lab pure water.

10.3 A *Duplicate (DUP)* analysis must be performed with each batch of maximum 20 samples and at a minimum of one per day.

10.3.1 The acceptance criteria are listed in the appropriate test code in LIMS.

10.3.2 DUP samples that fail to meet the acceptance criteria are automatically flagged in LIMS with a "R" qualifier.

10.3.3 If the acceptance criteria are not met, reanalyze. If the reanalysis fails the acceptance criteria document the failure with a CAR form. This is considered a significant affect on the data requiring client notification through the Case Narrative feature on the analytical report.

11.0 CALIBRATION AND STANDARDIZATION

11.1 Balance calibration and daily verification must be performed in accordance with the requirements of the Daily Balance Calibrations SOP.

11.2 Thermometer verification must be performed in accordance with the requirements of the Thermometer Calibration and Use SOP.

12.0 PROCEDURE

Analytical data for Specific Gravity is documented and retained using the Specific Gravity raw data sheet (copy attached). Analytical data for Density is documented and retained using the Miscellaneous Wet Chemistry logbook.

SPECIFIC GRAVITY

12.1 Record the temperature of the DI water as well as the samples to be analyzed. Rinse the thermometer with 1:1 HCl and DI water between samples.

12.2 Place a plastic cup on the balance then, using a volumetric pipette, add 10.0-ml DI water to the cup.

12.3 Record the weight of the blank then repeat with a second volume of water. Record all weights to the nearest 0.01g. The weight of the DI water should be 10.00 grams. If the average weight is not 10.00 grams, the balance calibration must have been affected or the volume measurement may be in error. Troubleshoot and reanalyze as appropriate.

12.4 Using clean plastic cups for each sample, repeat the steps taken for the DI water, substituting sample for the DI water.

DENSITY

12.5 Place a graduated cylinder on the balance and tare the balance.

12.6 Transfer an amount of sample into the cylinder so that you can measure the volume of sample added. Using the applicator stick or spatula, compact the sample to remove any air pockets that may be present. There is no need, however, to apply extensive pressure to pack the sample into the cylinder.

12.6.1 Note: although the concept of measuring a "volume" of a solid sample is unusual but exactly what is required for this application. By definition, the density of a solid sample is the mass of the sample that will fill a space equivalent to a measured volume of water.

12.7 Record the volume and weight of the sample. Record all weights to the nearest 0.01g.

13.0 CALCULATIONS AND DATA HANDLING

13.1 Calculate the Specific Gravity of the sample as follows:

$SG_{T/4}{}^{\circ}C$ = (Avg. Wt. Of Sample, g) (CF) / (Avg. Wt. Of DI Water, g)

Where: CF = the temperature correction factor from the table below

Correction Factor Table			
Temp (°C)	CF*	Temp (°C)	CF*
15	0.9991	35	0.9941
20	0.9982	40	0.9922
25	0.9975	45	0.9903
30	0.9957		
*Use factor from closest temperature			

13.2 Calculate the Density of the sample as follows:

Density, g/ml = (Wt. Of Sample, g) / (Volume Of Sample, ml)

13.3 After review, enter final results into the LIMS system. Details on the procedure for entering analytical data are in the Analytical Data Entry – Wet Chemistry SOP.

14.0 METHOD PERFORMANCE

14.1 Initial Demonstration of Capability and Method Detection Limit studies are not applicable to this procedure.

15.0 POLLUTION PREVENTION

15.1 Not applicable.

16.0 WASTE MANAGEMENT

16.1 Refer to the Sample Disposal SOP for guidance on the disposal of any resulting residue, digestate, distillate, extract or standard.

17.0 REFERENCES

17.1 Standard Methods Method 2710F, 18th ED

17.2 Microbac Laboratories Quality Assurance Plan, current revision, all sections

18.0 TABLES, FORMS, CHECKLISTS, AND OTHER ATTACHMENTS

Copy of the Specific Gravity raw data sheet (1 page)

Microbac Laboratories - Chicagoland Division

SPECIFIC GRAVITY - Method SM2710 F

Date/Time: ____________ Analyst: ____________ Balance ID: ______ Reviewed By: ____________

Sample ID	Cont ID	Sample Temp (°C)	Sample Volume (mL)	Wt. #1 of Sample (g)	Wt. #2 of Sample (g)	Average Wt. (g)	Correction Factor	Specific Gravity (T/4°C)

QC check performed by/date (problems noted on back): ____________ Reviewed By/Date: ____________

Date/Time: ____________ Analyst: ____________ Balance ID: ______ Reviewed By: ____________

Sample ID	Cont ID	Sample Temp (°C)	Sample Volume (mL)	Wt. #1 of Sample (g)	Wt. #2 of Sample (g)	Average Wt. (g)	Correction Factor	Specific Gravity (T/4°C)

QC check performed by/date (problems noted on back): ____________ Reviewed By/Date: ____________

Date/Time: ____________ Analyst: ____________ Balance ID: ______ Reviewed By: ____________

Sample ID	Cont ID	Sample Temp (°C)	Sample Volume (mL)	Wt. #1 of Sample (g)	Wt. #2 of Sample (g)	Average Wt. (g)	Correction Factor	Specific Gravity (T/4°C)

QC check performed by/date (problems noted on back): ____________ Reviewed By/Date: ____________

$$\text{Specific Gravity} = \frac{\text{Average Wt. Of Sample (g)}}{\text{Average Wt. Of Water (g)}} * \text{Correction Factor}$$

revision: _b_12-02

Correction Factor Table			
Temp (°C)	Corr. Fact.	Temp (°C)	Corr. Fact.
15	0.9991	35	0.9941
20	0.9982	40	0.9922
25	0.9975	45	0.9903
30	0.9957		

STANDARD OPERATING PROCEDURE FOR ACIDITY USING SM METHOD 2310 B AND EPA METHOD 305.1

Originating Author: Troy Goehl
Revision Author:

This SOP is effective upon signed approval by the following:

Troy M. Goehl
Unit Supervisor — 11/17/05 Date

Jeffrey M. Lucas
QA/QC Manager — 11/17/2005 Date

DISCLAIMER: This SOP has been developed for use at the Microbac Laboratories, Merrillville, Indiana facility. It is intended for use by trained analysts. As written, this SOP may not be specifically applicable to the activities of other organizations.

Last Review Date:
No Changes Needed
Approved By:

1.0 TABLE OF CONTENTS

2.0 SCOPE AND APPLICATION

2.1 This is a titrimetric procedure for the determination of Acidity. This procedure is applicable to the analysis of aqueous and drinking water matrix samples as well as solid matrix samples. The routine reporting limit (PQL) is 10 mg/L as $CaCO_3$ (400 mg/Kg as $CaCO_3$ based on a 1:40 sample preparation).

3.0 SUMMARY

3.1 The pH of a measured volume of sample is lowered with sulfuric acid. The sample is then oxidized with hydrogen peroxide and titrated with 0.1N sodium hydroxide to an endpoint of pH 8.3. For solid samples, a measured amount of sample is extracted with lab pure water then oxidized and titrated in the same manner as a water sample.

3.2 This procedure is based on the reference methods listed in section 17 of this document. This procedure contains no significant deviations from the reference methods. The reference methods are intended for the analysis of water samples. This procedure includes a modification so to analyze samples of a solid (soil) matrix.

4.0 DEFINITIONS

4.1 A list of definitions is in the Quality Assurance Plan.

4.2 The acidity of a water is defined as its capacity to react with a strong base to a designated pH. As such, the acidity value will change if the pH endpoint is changed.

5.0 INTERFERENCES

5.1 Dissolved gases that contribute to acidity or alkalinity (e.g. carbon dioxide, hydrogen sulfide, ammonia) can adversely affect the analytical results. These affects can occur during sampling, storage and/or analysis. Such affects are minimized by prompt titration to the endpoint after opening the sample container, avoiding vigorous sample shaking and minimizing the exposure of the sample to the atmosphere.

5.2 Samples containing hydrolyzable metal ions or reduced forms of polyvalent cations require pretreatment with hot peroxide prior to titration.

6.0 SAFETY

6.1 Consult the current revision of the Chemical Hygiene Plan.

6.2 Caution must be used when working with the 30% peroxide in the pretreatment steps.

7.0 EQUIPMENT AND SUPPLIES

The following is a list of materials needed to perform the steps of this procedure as written. See the reference method(s) for equipment and supply specifications.

7.1 All volumetric glassware used shall be ASTM Class A. Class B glassware must be verified for accuracy on an annual basis and labeled with an appropriate correction.

7.2 pH meter (refer to the pH SOP for details)

7.3 Graduated cylinder capable of measuring sample volume

7.4 Top loading or analytical balance capable of ±0.01g sensitivity

7.5 TCLP tumbler or stir plate with suitable containers for each

7.6 Filter paper: 12.5-cm, 934-AH or equivalent

7.7 Funnels or other filtering apparatus

7.8 Beakers or conical flasks

7.9 Stir plate and stir bars

7.10 Burette: 50-ml with 0.1-ml graduations and a 10-ml burette with 0.05-ml graduations

8.0 REAGENTS AND STANDARDS

8.1 All reagents used must be analytical reagent (AR) grade or higher. All standards must be traceable to NIST, when available. Certificates of traceability must be obtained from the manufacturer. All reagents and standards must be documented in the appropriate preparation logbook. Refer to the requirements in the Labeling of Standards, Reagents, Digestates and Extracts SOP.

8.2 Reagents

8.2.1 Lab pure water (DI water): Analyte free water is prepared as described in the Quality Assurance Plan. DI water may be obtained from any of the designated taps throughout the lab.

8.2.2 Sulfuric acid, concentrated: Fisher catalog # A300-212 or equivalent. Store this reagent in the cabinets located in the Wet Chemistry lab.

8.2.3 Sulfuric acid, 0.02N H_2SO_4: Fisher catalog # SA226-1 or equivalent. Store this reagent in the cabinets located in the Wet Chemistry lab.

8.2.4 Hydrogen peroxide, 30%: Fisher catalog # H325-500 or equivalent. Store this reagent in the cabinets located in the Metals Preparation lab.

8.2.5 Titrant, 0.1N NaOH: Fisher catalog # SS276-1 or equivalent is a titrant of a certified normality. Titrant must be used prior to manufacturer's expiration date. Store this titrant in the reagent cabinets in the Wet Chemistry lab.

8.2.6 pH Buffers: Standard buffers of pH 4, 7, and 10. Fisher catalog #SB101-500, SB107-500, and SB115-500, respectively. Equivalent products from other vendors may be substituted. Store these buffers in the main wet chemistry lab.

8.3 Standards

8.3.1 None

9.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

9.1 The client or other trained personnel collect samples. Samples received at the laboratory are considered representative unless otherwise noted.

9.2 Samples should be collected in a clean plastic or glass container. Preservation consists of storage in the range of 0.1-6°C. Samples are stored in the storage coolers located in the Sample Receiving area. Samples that fail to meet the preservation criteria are noted as such on the Cooler Inspection Report in the Login process.

9.3 Analysis must be performed within the maximum allowable hold time of 14-days from collection.

10.0 QUALITY CONTROL

10.1 An *Initial Demonstration of Capability* study must be performed prior to the initial analysis for each analyst and whenever substantial change has occurred in the procedure or instrument. Refer to the Capability and Detection Limit Studies SOP for details.

10.2 A *Method Blank* must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per day.

10.2.1 The acceptance criteria are < PQL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis, investigate and correct as needed or report data with an appropriate qualifier.

10.2.2 MBLKs that fail to meet the acceptance criteria cause the sample results to be automatically flagged in LIMS with a "B" qualifier.

10.2.3 The reporting of data associated with a failed control sample must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.2.4 Samples associated with a MBLK that fails with positive bias can be reported without narration if the sample concentration is < PQL or greater than 10 times the blank contamination.

10.3 *Duplicate* analysis must be performed with each batch of maximum 20 samples per matrix and at a minimum of one per day.

10.3.1 Acceptance criteria are listed in the appropriate test code in LIMS. The RPD criteria are applicable only to concentrations greater than 5-times the PQL. Values less than 5-times the PQL are considered acceptable if the absolute difference between the values is less than the PQL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria initiate a CAR and report the data set yielding the best precision.

10.3.2 DUP's that fail to meet the acceptance criteria are automatically flagged in LIMS with a "R" qualifier.

10.3.3 The reporting of data associated with a failed DUP must be documented with a CAR form. Client notification is required and can be accomplished using the Case Narrative of the report.

11.0 CALIBRATION AND STANDARDIZATION

11.1 Standard titrants are purchased certified from the vendor and do not require re-standardization provided they are used within the vendor-supplied expiration date.

11.2 If used, the balance must be calibrated and verified per the requirements of the Daily Balance Calibration SOP.

11.3 The pH meter must be calibrated prior to use. Refer to the pH SOP for details.

11.4 If the graduated cylinder used to measure sample volume or the buret used for titration are Class B glassware they must be verified for accuracy on an annual basis and labeled with an appropriate correction.

12.0 PROCEDURE

Analytical data is documented and retained using the Miscellaneous Titrations logbook. The traceability data for all reagents used must be documented. Analytical data must be

maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

AQUEOUS SAMPLES

12.1 Using a graduated cylinder, transfer 50-ml (or another appropriate volume) of sample into a titration vessel (beaker or flask).

12.2 Using a pH meter, measure the pH of the sample. If the pH > 4.0, add 5-ml increments of 0.02N H_2SO_4 until the pH drops below 4.0. Document the volume of acid used to lower the pH. If the sample pH < 4.0, no acid addition is necessary.

12.3 Add 5-drops of 30% H_2O_2 and boil for 2-5 minutes then allow the sample to cool to room temperature.

12.4 Fill a buret with titrant. Dispense any excess titrant so that the volume is at or below the 0-ml graduation. Document the start volume.

12.5 Insert a stir bar into the titration vessel, place the vessel on the stir plate and turn the stir plate on.

12.6 Place the pH electrode in the sample and allow the reading to stabilize.

12.7 Measure and record the pH.

12.8 Titrate to pH = 8.3 $\pm$ 0.2. As the end point is approached, make smaller additions of titrant and allow the pH meter to stabilize prior to making the next addition of titrant.

12.8.1 NOTE: It is optimum to use between 3 and 15-ml of titrant. If the 50-ml buret and the 0.1N titrant are used and less than 3-ml of titrant is required to reach the endpoint, use a larger sample size or a 10-ml buret with smaller graduations. If the 50-ml buret and the 0.1N titrant are used and more than 15-ml of titrant is required to reach the endpoint, use a lesser sample size or a more concentrated titrant.

SOLID SAMPLES

12.9 Prepare a 1:40 dilution (e.g. 2.5g per 100-ml or 25g per 1L) of the sample using lab pure water. The amount of sample used/prepared will depend on other tests that also need to be performed on the resulting water extract. Using the TCLP tumbler or stir plate as appropriate, mix the sample slurry for 2-hours then filter the sample using a 934-AH filter paper.

12.10 Follow the procedural steps as described above for an aqueous sample.

13.0 CALCULATIONS AND DATA HANDLING

13.1 Calculate the sample concentration as follows:

$$\text{Total Acidity, mg/L as } CaCO_3 = \frac{[(V_{titrant,\ ml})(N_{titrant}) - (V_{H2SO4,\ ml})(N_{H2SO4,\ ml})] * 50000}{\text{ml sample}}$$

Total Acidity, mg/Kg as $CaCO_3$ = Acidity, mg/L * PFac

13.2 After review, enter final results into the LIMS system. Details on the procedure for entering analytical data are in the Analytical Data Entry – Wet Chemistry SOP.

14.0 METHOD PERFORMANCE

14.1 An *Initial Demonstration of Capability* study is not applicable due to the absence of a suitable standard.

15.0 POLLUTION PREVENTION

15.1 The quantity of chemicals purchased should be based on expected usage during their shelf life and the disposal cost of unused material.

15.2 Prepare the minimum amount of reagent and standard necessary.

16.0 WASTE MANAGEMENT

16.1 Refer to the Sample Disposal SOP for guidance on the disposal of any resulting residue, digestate, distillate, extract or standard.

17.0 REFERENCES

17.1 Standard Methods Method 2310B, 18th ED

17.2 USEPA Method 305.1, revised 1974

17.3 Microbac Laboratories Quality Assurance Plan, current revision, all sections

18.0 TABLES, FORMS, CHECKLISTS, AND OTHER ATTACHMENTS

None

STANDARD OPERATING PROCEDURE FOR TOTAL AND REACTIVE SULFIDE

Originating Author: Allison Grieff
Revision Author:

This SOP is effective upon signed approval by the following:

Troy M Gohl — Unit Supervisor — 7-7-2004 — Date

Jeffrey M. Lacue — QA/QC Manager — 7.7.2004 — Date

DISCLAIMER: This SOP has been developed for use at the SIMALABS International, Merrillville, Indiana facility. It is intended for use by trained analysts. As written, this SOP may not be specifically applicable to the activities of other organizations.

1.0 TABLE OF CONTENTS

2.0 SCOPE AND APPLICATION

2.1 This is a colorimetric procedure for the determination of Sulfide. This procedure is applicable to the direct analysis for total sulfide in a water sample, the colorimetric finish portion for the analysis total sulfide in a solid sample, as well as colorimetric finish portion for the analysis reactive sulfide. The routine reporting limits (PQLs) are listed in the table below.

ANALYTE	PQL	
Total Sulfide	0.05 mg/l	0.25 mg/kg
Reactive Sulfide	50 mg/l	50 mg/kg

3.0 SUMMARY

3.1 Hydrogen sulfide as well as acid-soluble metal sulfides react with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. Measured at 670-nm, the intensity of the blue color is proportional to the sulfide concentration.

3.2 Water samples for total sulfide analysis are prepared by precipitating the sulfide with zinc acetate and removing the interferents that remain in the aqueous layer. Solid samples for total sulfide analysis are prepared by distillation with acid and collection of the analyte in a sodium hydroxide scrubber solution (identical to the preparation of samples for cyanide analysis). Samples for reactive sulfide are prepared by vacuum distillation with collection of the analyte in a sodium hydroxide scrubber.

3.3 The linear working range is 0.05 – 1.0 mg/l.

4.0 DEFINITIONS

4.1 Accuracy – The degree of agreement of a measured value with the true or expected value of the quantity of concern (% recovery of a known spiked analyte).

4.2 Aliquot – A measured portion of a sample, or solution, taken for sample preparation or analysis.

4.3 Analyte – The specific component measured in a chemical analysis For this procedure, the analyte is Sulfide as S.

4.4 Analytical Batch – A group of samples which are analyzed, at the instrument level, together using the same method, reagents and apparatus within the same time period. Typically, these are samples in the same RunID in the LIMS.

4.5 Blank – An artificial sample designed to assess specific sources of laboratory contamination. There are several types of blanks, which monitor a variety of processes:

- Calibration Blank – An aliquot of the standard diluent (lab pure water) that is not carried through the sample preparation scheme. It is analyzed to verify that the analytical system is free from contamination. Also referred to as an instrument blank.

- Method Blank – An aliquot of lab pure water taken through sample preparation (when required) and analysis. It is a test for contamination in sample preparation and analyses. Also referred to as a Procedural Blank.

4.6 Bias – The deviation of a measured value from a known or accepted value due to matrix effects or method performance. Bias may be determined quantitatively to correct measured values. Bias may be positive or negative.

4.7 Calibration – The establishment of an analytical curve based on the absorbance of known standards. The calibration standards must be prepared using the same type and concentration of reagents used in the sample preparation.

4.8 Continuing Calibration Verification Standard (CCV) – A standard used to verify the continued acceptability of the initial calibration curve. A continuing calibration verification must be repeated at the beginning and end of each analytical batch and every 10 samples, whichever is more frequent. The concentration of a verification standard shall be varied within the established calibration range. To meet this requirement the CCV is prepared at a concentration different than the ICV.

4.9 Detection Limit – The smallest concentration/amount of some component of interest that can be measured by a single measurement with a stated level of confidence.

- MDL – Method detection limit. The minimum concentration of a substance that can be measured and reported with a 99% degree of confidence. MDLs are determined by analyzing a minimum of seven consecutive standards that have been processed through all preparatory steps.

- PQL – The Practical Quantitation Limit is the lowest concentration that can reliably be achieved within specified limits of precision and accuracy during routine laboratory operating conditions. Typically, the PQL is a value in the range of 5 - 10 times the MDL. This is the reporting limit and is also referred to as the Estimated Quantitation Limit (EQL).

4.10 Initial Calibration Verification (ICV) – A standard used to verify the accuracy of calibration standards. Prepared from a second source than that of the calibration standards, its known value is measured against the calibration curve. This determines the integrity of working standards. Also referred to as an external verification standard or check standard.

4.11 Holding Time – The maximum storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

4.12 Laboratory Control Sample (LCS) – An aliquot of laboratory pure reagent spiked with target analyte. The sample is carried through the entire analytical process and analyte recovery is used to monitor method performance. Also referred to as a laboratory fortified blank (LFB).

4.13 Laboratory Control Sample Duplicate (LCSD) – An aliquot of laboratory pure reagent spiked with the identical amount of target analyte as the LCS. Results of the two spikes are used to assess both the bias and precision of a method with a given sample matrix. Also referred to as a laboratory fortified blank duplicate (LFB DUP).

4.14 Matrix – The component or substrate which may contain the analyte of interest. Matrices are limited to the following: aqueous (includes extracts from the TCLP or other extraction procedure, groundwater, surface water, and wastewater), drinking water (potable water and laboratory pure water), non-aqueous liquid (organic liquid having <15% settleable solids), and solid (includes sediment, sludge, and soil).

4.15 Matrix Spike (MS) – An aliquot of a sample that is spiked with a known amount of target analyte. Recovery of the matrix spike, expressed as percent recovery, is used to assess the bias of a method in a given sample matrix. Also referred to as a laboratory fortified sample matrix (LFSM).

4.16 Matrix Spike Duplicate (MSD) – An aliquot of the same sample used for the MS, spiked with the identical amount of target analyte as the MS. Results of the two spikes are used to assess both the bias and precision of a method with a given sample matrix. Also referred to as a laboratory fortified sample matrix duplicate (LFSM DUP).

4.17 Percent Recovery – A measure of accuracy that is calculated as the measured value relative to the true value, expressed as a percent.

$$\%R = \frac{MV}{TV} * 100$$

where: MV = measured value
TV = true value

4.18 Precision – The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions. It is concerned with the comparability of results from duplicate or replicate analyses. (%RPD between the recoveries of two known analyte spikes, and %RSD between the recoveries of three or more measurements).

4.19 Preparation Batch – A group of samples of similar composition which are prepared together using the same method, reagents and apparatus within a 24-hour calendar day or every 20 samples, whichever is more frequent. Typically, these are samples in the same Batch ID in the LIMS.

4.20 Preservative – A reagent added to a sample, or an action used, to prevent or slow decomposition or degradation of a target analyte or a physical process. Thermal and chemical preservation may be used in tandem to prevent sample deterioration.

4.21 Relative Percent Difference (% RPD) – Used to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

$$\% \text{ RPD} = \frac{|X - Y|}{(X + Y) / 2} * 100$$

where: X = value 1
Y = value 2

4.22 Sample – A portion of material to be analyzed.

- Environmental sample – sample supplied by the client for analysis.
- QC sample – sample prepared in the lab analyzed to assess the bias/precision of the analytical system.

4.23 Sample Duplicate – Two aliquots of the same sample processed independently. This monitors precision of the analysis. Precision results are reported as relative percent difference (RPD).

5.0 INTERFERENCES

5.1 Strong reducing agents interfere by preventing formation of the blue color. These interferents are removed by precipitating ZnS and replacing the supernatant with DI water as described in the procedure.

5.2 Ferrocyanide interferes by producing a blue color.

6.0 SAFETY

6.1 Eye protection must be worn at all times while in the laboratory.

6.2 Lab coats and gloves are recommended. Avoid direct contact with reagents, standards, and/or samples.

6.3 Consult the Material Safety Data Sheets (MSDS) for each chemical used for information regarding fire hazard, toxicity, first aid, storage, disposal, spill procedures, and recommended protective equipment.

6.4 Chemicals having the potential to produce toxic fumes must be handled in a fume hood.

7.0 EQUIPMENT AND SUPPLIES

The following is a list of materials needed to perform the steps of this procedure as written. See the reference method(s) for equipment and supply specifications.

7.1 All volumetric glassware used shall be ASTM Class A.

7.2 Volumetric flasks: 10-ml and 500-ml

7.3 Pipettes: various volumes

7.4 Vortex mixer

7.5 Spectrophotometer and cuvettes

8.0 REAGENTS AND STANDARDS

8.1 All reagents used must be analytical reagent (AR) grade or higher. All standards must be traceable to NIST, when available. Certificates of traceability must be obtained from the manufacturer. All reagents and standards must be documented in the appropriate preparation logbook. Refer to the requirements in the Labeling of Standards, Reagents, Digestates and Extracts SOP.

8.2 Reagents

8.2.1 Lab pure water: Analyte free water is available via dedicated taps throughout the lab and is prepared as described in the Quality Assurance Plan.

8.2.2 Sodium Hydroxide, NaOH: Fisher catalog #S318-3 or equivalent

8.2.3 0.25N NaOH: Dissolve 40g sodium hydroxide in approximately 3.5L DI water. Dilute to a final volume of 4L with DI water. Transfer this reagent into a plastic bottle and store in the main wet chemistry lab.

8.2.4 Sulfide 1 Reagent: Hach catalog #1816-32. Store this reagent in the main wet chemistry lab.

8.2.5 Sulfide 2 Reagent: Hach catalog #1817-32. Store this reagent in the main wet chemistry lab.

8.3 Standards

8.3.1 Sodium Sulfide: Na_2S $9H_2O$, Fisher catalog #S425-500 or equivalent

8.3.2 Stock Calibration Standard, 500 mg/l as S: In a 500-ml volumetric flask, dissolve 1g NaOH with approximately 250-ml DI water then dissolve and dilute 1.873g (±0.002g) sodium sulfide to the mark with DI water. Transfer this into a plastic bottle and store in the standards cooler in the wet chemistry lab.

8.3.3 Working Spike Standard, 50 mg/l as S: In a cuvette, dilute 1.0-ml of the stock calibration standard to 10-ml with 0.25N NaOH. Prepare this standard fresh each day of analysis. This standard is used to prepare the calibration curve, the MS/MSD's for total sulfide in water samples, and the PDS samples for all matrices.

8.3.4 Calibration Standards: In individual cuvettes, prepare the following standards by diluting volumes of the working spike standard to 10-ml with 0.25N NaOH.

Vol Working Std, ml	Conc, mg/l
0	0
0.01	0.05
0.02	0.10
0.04	0.20
0.10	0.50
0.15	0.75
0.20	1.0

8.3.5 MS/MSD, 0.5 mg/l as S (*for total sulfide in water*): In a cuvette, dilute 0.1-ml of the working spike standard to 10-ml with sample. Preparation and concentration of the LCS/MS/MSD for reactive sulfide and total sulfide in a solid are found in the respective preparation SOP.

8.3.6 PDS, 0.5 mg/l as S: In a cuvette, dilute 0.1-ml of the working spike standard to 10-ml with sample.

8.3.7 Stock Verification Standard, 500 mg/l as S: In a 500-ml volumetric flask, dissolve 1g NaOH with approximately 250-ml DI water then dissolve and dilute 1.873g (±0.002g) sodium sulfide to the mark with DI water. Transfer this into a plastic bottle and store in the standards cooler in the wet chemistry lab. **NOTE:** as this standard is prepared from the same material as the calibration standard (due to limited options) two separate analysts must prepare these standards (i.e. analyst A prepares the Stock Calibration while analyst B prepares the Stock Verification).

8.3.8 Working Verification Standard, 50 mg/l as S: In a 10-ml volumetric flask, dilute 1.0-ml of the stock verification standard to the mark with 0.25N NaOH. Prepare this standard fresh each day of analysis.

8.3.9 ICV, 0.25 mg/l as S: In a cuvette, dilute 0.05-ml of the working verification standard to 10-ml with 0.25N NaOH. Prepare this standard fresh each day of analysis.

8.3.10 CCV, 0.50 mg/l as S: In a cuvette, dilute 0.1-ml of the working verification standard to 10-ml with 0.25N NaOH. Prepare this standard fresh for each verification.

9.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

9.1 The client or other trained personnel collect samples. Samples received at the laboratory are considered representative unless otherwise noted.

9.2 Water samples for Total Sulfide: should be collected in a plastic container. Preservation consists of sodium hydroxide to a pH > 9 in tandem with zinc acetate, and storage in the range of 0.1-6°C. Samples are stored in the coolers in the sample receipt area. Samples that fail to meet the preservation criteria are noted as such on the Cooler Inspection Report in the Login process.

9.3 Solid samples for Total Sulfide: should be collected in a glass or plastic container. Preservation consists of storage in the range of 0.1-6°C. Samples are stored in the coolers in the sample receipt area. Samples that fail to meet the preservation criteria are noted as such on the Cooler Inspection Report in the Login process.

9.4 Samples for Reactive Sulfide: should be collected in a glass or plastic container. Preservation consists of storage in the range of 0.1-6°C. Samples are stored in the coolers in the sample receipt area. Samples that fail to meet the preservation criteria are noted as such on the Cooler Inspection Report in the Login process.

9.5 Preparation and analysis must be performed within the maximum allowable hold time of 7-days from collection. LIMS automatically flags data with a "H" qualifier if analyzed past the maximum hold time.

10.0 QUALITY CONTROL

10.1 An *Initial Demonstration of Capability* study must be performed prior to the initial analysis for each analyst and whenever substantial change has occurred in the procedure or instrument. Analyze four separate standards prepared in the range of 8-10 times the method detection limit listed in section 14.0. These standards must be from a source different from that used for calibration and taken through the entire analytical procedure. Submit the data to the QA department for evaluation. Refer to the Capability and Detection Limit Studies SOP for details.

10.2 A *Method Detection Limit* study must be performed for each new procedure, annually thereafter, and whenever a change in instrument occurs. Analyze a minimum of seven (maximum of ten) standards prepared in the range of 2-5 times the method detection limit listed in section 14.0 or an estimated detection limit. These standards must be taken through the entire analytical procedure. Submit the data to the QA department for evaluation. Refer to the Capability and Detection Limit Studies SOP for details.

10.3 A *Calibration Verification Standard* must be analyzed immediately after calibration, before the first sample, after every 10 samples, and after the sample. The concentration of the ICV must be different than that of the CCV. Acceptance criteria are the statistical limits of 82.0-118% recovery. If acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier. Samples associated with a verification that fails with positive bias can be reported if the sample concentration is a non-detect. ICV and CCV standards that fail to meet the

acceptance criteria are automatically flagged in LIMS with a "S" qualifier. The reporting of data associated with a failed control sample must be documented with a CAR form.

10.4 A *Calibration Verification Blank* sample must be analyzed after each calibration verification standard. The acceptance criteria are < PQL. Analysis for compliance with our Wisconsin DNR certification must be evaluated down to the current MDL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate. If the blank does not meet the acceptance criteria, all samples < PQL or greater than 10 times the blank contamination may be reported. All other environmental samples must be reanalyzed or reported with an appropriate qualifier in the Case Narrative of the report. The reporting of data associated with a failed control sample must be documented with a CAR form.

10.5 A *Method Blank* must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per day. Acceptance criteria are < PQL. Analysis for compliance with our Wisconsin DNR certification must be evaluated down to the current MDL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate. If the blank does not meet the acceptance criteria, all samples < PQL or greater than 10 times the blank contamination may be reported. All other environmental samples must be reanalyzed or reported with a "B" qualifier, which is automatically applied in the LIMS. The reporting of data associated with a failed control sample must be documented with a CAR form.

10.6 A *Laboratory Control Sample* is prepared with each batch of maximum 20 samples and at a minimum of one per day for total sulfide in a solid and reactive sulfide. A LCS for total sulfide in water is not applicable, as there is no distillation/digestion preparation. Acceptance criteria are the statistically generated limits of 10.0-161% recovery (total in a solid) or 52.2-138% recovery (reactive sulfide) as appropriate. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria all environmental samples must be reprepared and analyzed or reported with an appropriate qualifier. If the LCS fails with high bias, samples having a non-detectable concentration may be reported without qualification. LCS's that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier. The reporting of data associated with a failed control sample must be documented with a CAR form.

10.7 A *Matrix Spike and Matrix Spike Duplicate* sample must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per day. Acceptance criteria for the MS/MSD are the statistically based limits of 61.1-149% recovery with a 20.0 RPD for total sulfide in waters, 10.0-149% recovery with a 20.0 RPD for total sulfide in solids, 10.0-170% recovery with a 20.0 RPD for reactive sulfide in waters, and 10.0-53.2% recovery with a 20.0 RPD for reactive sulfide in solids. If the acceptance criteria for either, accuracy or precision, are not met, reanalyze. If reanalysis is performed and fails to meet the acceptance criteria the sample and its MS/MSD must be reprepared and analyzed or reported with an appropriate qualifier. If the concentration measured in the sample is greater than 4-times the concentration of the spike, the spike amount used is insufficient and

the MS/MSD not applicable. MS/MSD's that fail to meet the accuracy criteria are automatically flagged in LIMS with a "S" qualifier. Those failing to meet the precision criteria are automatically flagged in LIMS with a "R" qualifier. The reporting of data associated with a failed control sample must be documented with a CAR form.

10.8 A *Post Digestion Spike* can be prepared to evaluate matrix interference for a sample that failed to meet the accuracy or precision criteria criteria in the MS/MSD. Acceptance criteria are the nominal limits of ≤20.0 RPD. A PDS that fails to meet the acceptance criteria is indicative of matrix interference. If the PDS fails with high bias, samples having a non-detectable concentration may be reported without qualification. PDS's that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier. The reporting of data associated with a failed control sample must be documented with a CAR form.

10.9 Details for the determination of statistical limits are in the Generation and Updating of Statistical Recovery Limits SOP.

11.0 CALIBRATION AND STANDARDIZATION

Calibration data is documented and retained using the Sulfide raw data sheet (copy attached).

11.1 Perform the required preventative maintenance as necessary.

11.2 A new calibration curve is required on an annual frequency and when the stock calibration standard is replaced.

11.3 Prepare a standard curve as detailed in section 8. Develop color as detailed in the Procedure section "ANALYSIS" below.

11.4 Enter the data into the WetChemCalibCurves.xls file. Acceptable calibration is achieved with a correlation coefficient ≥ 0.995. The spreadsheet evaluates the calibration data and indicates whether or not the calibration requirement has been met. Analysis of environmental samples cannot proceed without the generation of an acceptable calibration.

12.0 PROCEDURE

Analysis data are documented and retained using the Sulfide raw data sheet (copy attached).

12.1 PREPARATION

12.1.1 This section describes the preparation of water samples for total sulfide analysis. Preparation of solid samples for total sulfide analysis as well as the preparation of samples for reactive sulfide analysis is described in their respective SOP.

12.1.2 Remove samples from the cooler and allow the precipitate to settle.

12.1.3 Mark the water level on the outside of the sample container.

12.1.4 Discard the supernatant by slowly/carefully pouring off this water layer. Do not loose the precipitate. The supernatant is not need for the analysis. As such, it can be poured directly into the sink or into a clean beaker or other container. Using a clean container to collect the supernatant provides a means to start over again in case some of the precipitate is poured out.

12.1.5 Replace the discarded supernatant volume with DI water by filling the sample bottle to the mark previously made.

12.1.6 The steps above may be repeated one more time if needed to remove additional/high concentrations of intereferents.

12.2 ANALYSIS

12.2.1 This section describes the color development procedure for measuring the following: total sulfide in a water sample as prepared above, total sulfide in the distillate prepared from a solid sample, reactive sulfide in the distillate prepared from a sample of any matrix.

12.2.2 Gently shake the sample/distillate. It is critical to suspend the precipitate when measuring total sulfide in a water sample as the precipitate is where the analyte, if present, is located.

12.2.3 Transfer 10-ml sample into a cuvette.

12.2.4 Add 0.4-ml Sulfide 1 Reagent and gently mix with the vortex mixer

12.2.5 Add 0.4-ml Sulfide 2 Reagent and gently mix with the vortex mixer.

12.2.6 Wait 5-minutes then measure the absorbance at 670-nm.

13.0 CALCULATIONS AND DATA HANDLING

13.1 Use the WetChemCalibCurves.xls file to calculate the aqueous analyte concentrations.

13.2 The sample concentration is calculated as follows. The LIMS will calculate the final concentration based upon the aqueous concentration measured at the instrument and the data from the preparation batch.

Conc, ppm = (conc, mg/l) (PFac) (DF)

Where: conc = aqueous concentration measured at the instrument
PFac = Final Vol, ml / sample size, ml or g
DF = dilution factor

13.3 The LIMS calculates the dry-weight concentration for solid samples as follows:

$$\text{Conc. Dry} = \frac{\text{(wet weight conc.)}}{\text{(100 - \%Moisture)}}$$

13.4 After review, enter final results into the LIMS system. Results flagged by the LIMS with an "E" qualifier are above the linear range of the instrument. There is less certainty in these data and, if sufficient sample and holding time are available, should be reanalyzed at an appropriate dilution. Details on the procedure for entering analytical data into the LIMS are in the Data Entry SOP.

14.0 METHOD PERFORMANCE

14.1 Initial Demonstration of Capability

A typical IDC study will yield data similar to:

n =	4	
Standard Deviation (σ_{n-1})	0.021	mg/l
Spiked Concentration	0.25	mg/l
Average Concentration	0.249	mg/l
Average Recovery	99.7	%

14 2 Method Detection Limit

The latest MDL study yielded the following data:

Total Sulfide in Water		
n =	10	
Standard Deviation (σ_{n-1})	0.007	mg/l
Spiked Concentration	0.1	mg/l
Average Concentration	0.105	mg/l
Average Recovery	105	%
Calculated MDL	0.02	mg/l

Total Sulfide in Solid		
n =	10	
Standard Deviation (σ_{n-1})	0.007	mg/kg
Spiked Concentration	0.04	mg/kg
Average Concentration	0.042	mg/kg
Average Recovery	106	%
Calculated MDL	0.02	mg/kg

Reactive Sulfide		
n =	10	
Standard Deviation (σ_{n-1})	0.056	ppm
Spiked Concentration	10	ppm
Average Concentration	0.83	ppm
Average Recovery	8.3	%
Calculated MDL	0.16	ppm

15.0 POLLUTION PREVENTION

15.1 The quantity of chemicals purchased should be based on expected usage during their shelf life and the disposal cost of unused material.

15.2 Prepare the minimum amount of reagent and standard necessary.

16.0 WASTE MANAGEMENT

16.1 Refer to the SIMALABS International Sample Disposal SOP for guidance on the disposal of any resulting residue, digestate, distillate, extract or standard.

17.0 REFERENCES

17.1 USEPA Method 376.2, revision 3/83

17.2 SW-846 Method 9030

17.3 SW-846 Method 7.3.4.2

17.4 Standard Methods Method 4500-S^{2-} C & D, 18th ED

17.5 Hach Chemical Company Method 8131

17.6 SIMALABS International Quality Assurance Plan, current revision

18.0 TABLES, FORMS, CHECKLISTS, AND OTHER ATTACHMENTS

Copy of the Sulfide raw data sheet (1 page)
Copy of Hach method 8131 (4 pages)

Microbac Laboratories - Simalabs Division
Sulfide - Method 376.2 / 9030 / 7.3.4.2

☐ Total
☐ Reactive

Analyst: _____ Date/Time: _____ Reviewed By/Date: _____

	STD ID	Exp. Date	True Value		Reagent ID	Exp. Date
ICV/CCV				Sulfide 1		
LCS/MS/MSD				Sulfide 2		
0.25 N NaOH						

Calibration Curve Reference:

Date: _____ Page #: _____

Book #: _____ r = _____

Sample ID	Cont ID	Sample Volume (mL)	Dilution Factor	Absorbance	Concentration mg/L

Sulfide

✔Method 8131

Methylene Blue Method*

(5 to 800 µg/L)

Scope and Application: For testing total sulfides, H_2S, HS^-, and certain metal sulfides in groundwater, wastewater brines, and seawater; USEPA Approved for reporting wastewater analysis**

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

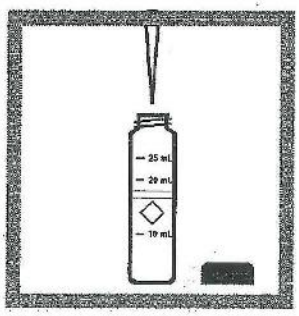
** Procedure is equivalent to USEPA method 376.2 and Standard Method 4500-S^{2-} D for wastewater.

Tips and Techniques

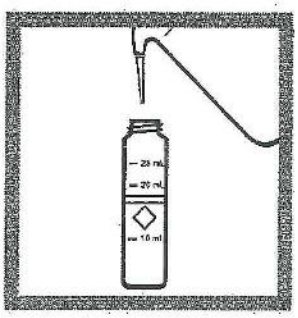
- Analyze samples immediately. Do not preserve for later analysis.
- Avoid excessive agitation of samples to minimize sulfide loss.
- Some sulfide loss may occur if dilution is necessary.
- Wipe the outside of sample cells before each insertion into the instrument cell holder. Use a damp towel followed by a dry one to remove fingerprints or other marks.
- Sulfide 2 reagent contains potassium dichromate. The final solution will contain hexavalent chromium (D007) at a concentration regulated as a hazardous waste by Federal RCRA. Please see *Section 5* for further information on proper disposal of these materials.

Method 8131

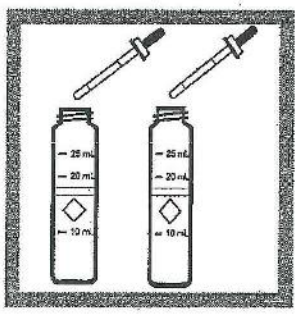
1. Touch **Hach Programs.** Select program **690 Sulfide.** Touch **OK.**



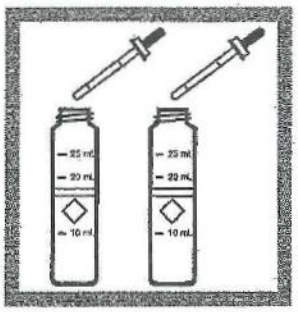
2. Avoiding excess agitation of the sample, use a pipet add 25 mL of sample to a sample cell (the prepared sample).



3. Measure 25 mL of deionized water into a second sample cell (the blank).



4. Use the calibrated 1-mL dropper to add 1.0 mL of Sulfide 1 Reagent to each cell. Swirl to mix.



5. Use the calibrated 1-mL dropper to add 1.0 mL of Sulfide 2 Reagent to each cell. Cap the cell and immediately invert to mix.

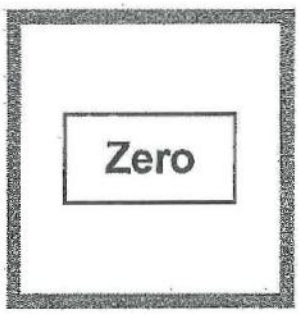
A pink color will develop, then the solution will turn blue if sulfide is present.

6. Touch the timer icon.

Touch **OK**.

A five-minute reaction period will begin.

7. When the timer beeps, wipe the blank and place it into the cell holder.



8. Touch **Zero**.

The display will show:

0 µg/L S^{2-}

9. Wipe the prepared sample and place it into the cell holder.

Results will appear in µg/L S^{2-}.

Determining Soluble Sulfides

Determine soluble sulfides by centrifuging the sample in completely filled, capped tubes and analyzing the supernatant. Insoluble sulfides are then estimated by subtracting the soluble sulfide concentration from the total sulfide result.

Interferences

Interfering Substance	Interference Levels and Treatments
Strong reducing substances (sulfite, thiosulfate and hydrosulfite)	Interfere by reducing the blue color or preventing its development
Sulfide, high levels	High concentrations of sulfide may inhibit full color development and require sample dilution Some sulfide loss may occur when the sample is diluted.
Turbidity	For turbid samples, prepare a sulfide-free blank as follows. Use it in place of the deionized water blank in the procedure. 1. Measure 25 mL of sample into a 50-mL Erlenmeyer flask. 2. Add Bromine Water (Cat. No. 2211-20) dropwise with constant swirling until a permanent yellow color just appears. 3. Add Phenol Solution (Cat. No. 2112-20) dropwise until the yellow color just disappears. Use this solution to replace the deionized water in *step 3* of the procedure.

Sample Collection, Storage, and Preservation

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Analyze samples immediately.

Method Performance

Precision

Standard: 275 µg/L S^{2-}

Program	95% Confidence Limits of Distribution
690	256–294 µg/L S^{2-}

See *Section 3.4.3 Precision* on page *53* for more information, or if the standard concentration did not fall within the specified range.

Sensitivity

Portion of Curve	ΔAbs	ΔConcentration
Entire range	0.010	5 µg/L S^{2-}

See *Section 3.4.5 Sensitivity* on page *54* for more information.

Summary of Method

Hydrogen sulfide and acid-soluble metal sulfides react with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration. High sulfide levels in oil field waters may be determined after proper dilution. Test results are measured at 665 nm.

Required Reagents

Description	Quantity required per test	Unit	Cat. No.
Sulfide Reagent Set (100 tests)			22445-00
Includes:			
(2) Sulfide 1 Reagent	2 mL	100 mL MDB	1816-32
(2) Sulfide 2 Reagent	2 mL	100 mL MDB	1817-32
Water, deionized	25 mL	4 liters	272-56

Required Apparatus

Pipet, volumetric, Class A, 25-mL	1	each	14515-40
Pipet Filler, safety bulb	1	each	14651-00
Sample Cells, 10-20-25 mL, w/cap	2	6/pkg	24019-06

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – Call toll-free 800-227-4224
Outside the U.S.A. – Contact the HACH office or distributor serving you.
On the Worldwide Web – www.hach.com; E-mail – techhelp@hach.com

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

7/03
Sulfide_None_Other_MLB_Eng_Ody.fm

STANDARD OPERATING PROCEDURE FOR AMMONIA – NITROGEN BY AUTOMATED PHENATE COLORIMETRY USING EPA METHOD 350.1 AND SM METHOD 4500-NH_3 G

Originating Author: Unknown
Revision Author: Nicole Rainwater

This SOP is effective upon signed approval by the following:

Troy Goehl — Unit Supervisor — 10/23/03 — Date

Jeffrey M. Lorenz — QA/QC Manager — 10.22.2003 — Date

DISCLAIMER: This SOP has been developed for use at the SIMALABS International, Merrillville, Indiana facility. It is intended for use by trained analysts. As written, this SOP may not be specifically applicable to the activities of other organizations.

1.0 TABLE OF CONTENTS

2.0 SCOPE AND APPLICATION

2.1 This is an automated colorimetric procedure for the determination of ammonia - nitrogen. This procedure is applicable to the analysis of aqueous, non-aqueous liquid, drinking water, solid matrix samples. The routine reporting limit is 0.1 mg/l as N.

3.0 SUMMARY

3.1 This method is based on Berthelot reaction. Ammonia reacts with alkaline phenol and subsequently with sodium hypochlorite to form indophenol blue. Sodium nitroprusside is added to enhance the sensitivity. The absorbance of the reaction product is measured at 630-nm and is directly proportional to the original ammonia concentration.

3.2 The linear working range is 0.1 – 20 mg/l as N.

4.0 DEFINITIONS

4.1 Accuracy – The degree of agreement of a measured value with the true or expected value of the quantity of concern (% recovery of a known spiked analyte).

4.2 Aliquot – A measured portion of a sample, or solution, taken for sample preparation or analysis.

4.3 Analyte – The specific component measured in a chemical analysis.

4.4 Analytical Batch – A group of samples which are analyzed, at the instrument level, together using the same method, reagents and apparatus within the same time period. Typically, these are samples in the same RunID in the LIMS.

4.5 Blank – An artificial sample designed to assess specific sources of laboratory contamination.

- Calibration Blank – An aliquot of the standard diluent that is not carried through the sample preparation scheme. It is analyzed to verify that the analytical system is free from contamination. Also referred to as an instrument blank.

- Method Blank – An aliquot of lab pure water taken through sample preparation and analysis. It is a test for contamination in sample preparation and analyses. Also referred to as a Preparation Blank.

4.6 Bias – The deviation of a measured value from a known or accepted value due to matrix effects or method performance. Bias may be determined quantitatively to correct measured values. Bias may be positive or negative.

4.7 Calibration – The establishment of an analytical curve based on the absorbance of known standards. The calibration standards must be prepared using the same type and concentration of acids, solvents, or other solutions used in the sample preparation.

4.8 Continuing Calibration Verification Standard (CCV) – A standard used to verify the continued acceptability of the initial calibration curve. Continuing calibration verification must be repeated after every 10 samples and at the end of each analytical batch. The concentration of the continuing calibration verification standard shall be varied from that of the ICV.

4.9 Detection Limit – The smallest concentration/amount of analyte that can be measured by a single measurement with a stated level of confidence.

- IDL – Instrument detection limit. A statistically determined detection limit used to estimate the instrument's sensitivity. The IDL is obtained by analyzing seven consecutive standards, without preparation, at a concentration of 3 – 5 times the estimated IDL. These standards must meet criteria of bias and precision.

- MDL – Method detection limit. The minimum concentration of a substance that can be measured and reported with a 99% degree of confidence. MDLs are determined by analyzing a minimum of seven consecutive standards that have been processed through all preparatory steps. These standards must meet criteria of bias and precision.

- PQL – The Practical Quantitation Limit is the lowest concentration that can reliably be achieved within specified limits of precision and accuracy during routine laboratory operating conditions. Typically, the PQL is a value in the range of 5 - 10 times the MDL. Also referred to as the Estimated Quantitation Limit (EQL).

4.10 Initial Calibration Verification (ICV) – A standard used to verify the accuracy of calibration standards. Prepared from a second source than that of the calibration standards, its known value is measured against the calibration curve. This determines the integrity of working standards. An initial calibration verification must be performed after calibration and before any samples are analyzed. The concentration of the ICV shall be varied from that of the CCV.

4.11 Holding Time – The maximum storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

4.12 Laboratory Control Sample (LCS) – An aliquot of laboratory pure reagent spiked with target analyte. The sample is carried through the entire analytical process and analyte recovery is used to monitor method performance. Also referred to as a laboratory fortified blank (LFB).

4.13 Laboratory Control Sample Duplicate (LCSD) – An aliquot of laboratory pure reagent spiked with the identical amount of target analyte as the LCS. Results of the two spikes are used to assess both the bias and precision of a method with a given sample matrix. Also referred to as a laboratory fortified blank duplicate (LFB DUP).

4.14 Matrix – The component or substrate which may contain the analyte of interest. Matrices are limited to the following: aqueous (includes extracts from the TCLP or other extraction procedure, groundwater, surface water, and wastewater), drinking water (potable water and laboratory pure water), non-aqueous liquid (organic liquid having <15% settleable solids), and solid (includes sediment, sludge, and soil).

4.15 Matrix Spike (MS) – An aliquot of a sample that is spiked with a known amount of target analyte. Recovery of the matrix spike, expressed as percent recovery, is used to assess the bias of a method in a given sample matrix. Also referred to as a laboratory fortified sample matrix (LFSM).

4.16 Matrix Spike Duplicate (MSD) – An aliquot of the same sample used for the MS, spiked with the identical amount of target analyte as the MS. Results of the two spikes are used to assess both the bias and precision of a method with a given sample matrix. Also referred to as a laboratory fortified sample matrix duplicate (LFSM DUP).

4.17 Percent Recovery – A measure of accuracy that is calculated as the measured value relative to the true value, expressed as a percent.

$$\%R = \frac{MV}{TV} * 100$$

where: MV = measured value
TV = true value

4.18 Precision – The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions. It is concerned with the comparability of results from duplicate or replicate analyses. (%RPD between the recoveries of two known analyte spikes, and %RSD between the recoveries of three or more measurements).

4.19 Preparation Batch – A group of samples of similar composition which are prepared together using the same method, reagents and apparatus within a 24 hour calendar day or every 20 samples, whichever is more frequent. Typically, these are samples in the same batch ID in the LIMS.

4.20 Preservative – A reagent added to a sample, or an action used, to prevent or slow decomposition or degradation of a target analyte or a physical process. Thermal and chemical preservation may be used in tandem to prevent sample deterioration.

4.21 Relative Percent Difference (% RPD) – Used to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an

absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

$$\% \text{ RPD} = \frac{|X - Y|}{(X + Y) / 2} * 100$$

where: X = value 1
Y = value 2

4.22 Sample – A portion of material to be analyzed.

- Environmental sample – sample supplied by the client for analysis.
- QC sample – sample prepared in the lab analyzed to assess the bias/precision of the analytical system.

5.0 INTERFERENCES

5.1 Calcium and magnesium ions may precipitate if present in sufficient concentrations; tartrate or EDTA can be added to the sample in-line in order to prevent this problem.

5.2 Color, turbidity and certain organic species can interfere. Most interference is removed through distillation. If samples are not distilled, turbidity and color can be removed by manual filtration or by running the samples through the manifold without color formation.

6.0 SAFETY

6.1 Eye protection must be worn at all times while in the laboratory.

6.2 Lab coats and gloves are recommended. Avoid direct contact with reagents, standards, and/or samples.

6.3 Consult the Material Safety Data Sheets (MSDS) for each chemical used for information regarding fire hazard, toxicity, first aid, storage, disposal, spill procedures, and recommended protective equipment.

6.4 Chemicals having the potential to produce toxic fumes must be handled in a fume hood.

7.0 EQUIPMENT AND SUPPLIES

7.1 All volumetric glassware used shall be ASTM Class A.

7.2 Oxford 1-5 ml and 5-10 ml autopipets

7.3 13 X 100 mm disposable borosilicate glass culture tubes

7.4 Lachat QuikChem 8000 FIA instrument including sampler, multichannel proportioning pump, reaction manifold, calorimetric detector, and data system.

7.5 Heating unit.

7.6 1 L distillation flasks and condenser units

7.7 Heating mantles

7.8 250-ml graduated cylinders

7.9 pH meter

7.10 Boiling stones

7.11 450-ml beakers

8.0 REAGENTS AND STANDARDS

8.1 All reagents used must be analytical reagent (AR) grade or higher. All standards must be traceable to NIST, when available. Certificates of traceability must be obtained from the manufacturer. All reagents and standards must be documented in the appropriate preparation logbook.

8.2 Reagents

8.2.1 Lab pure water

8.2.2 Sodium Phenolate. Dissolve 88-ml of 88% liquefied phenol in approximately 600-ml water in a 1 L volumetric flask. While stirring, slowly add 32g NaOH. Cool, dilute to mark, and invert to mix.

8.2.3 Sodium Hypochlorite. Dilute 250-ml Clorox Bleach to mark of 500-ml volumetric flask with water. Invert to mix.

8.2.4 Buffer. In a 1 L volumetric flask, dissolve 50.0g disodium ethylenediamine tetraacetate and 5.5g NaOH in about 900-ml water. Dilute to mark and invert to mix.

8.2.5 Sodium Nitroprusside. Dissolve 3.5g sodium nitroprusside in a 1 L volumetric flask.

8.2.6 Sulfuric Acid, concentrated

8.2.7 1 N H_2SO_4: In a 1L volumetric flask, dilute 28-ml conc. H_2SO_4 to the mark with DI water.

8.2.8 0.04 N H_2SO_4: In a 1L volumetric flask, add 40-ml of 1 N H_2SO_4. Dilute to mark with reagent water and invert to mix.

8.3 Standards

8.3.1 Stock Calibration Standard, 1000 ppm as N

8.3.2 Working Calibration Standard, 20 ppm as N: In a 500-ml volumetric flask, dilute 10.0-ml of stock calibration standard to the mark with DI water.

8.3.3 Stock Verification Standard, 1000 ppm as N: This standard must be of a separate source or lot number from that used for calibration.

8.3.4 Working Verification Standard, 100 ppm as N: In a 500-ml volumetric flask, dilute 50.0-ml of the stock verification standard to the mark with DI water.

8.3.5 LCS/MS, 2.0 ppm as N: Add 5.0-ml of the working verification standard to 250-ml of DI water or sample to prepare a LCS or MS, respectively.

8.3.6 ICV, 5.0 mg/l as N: Dilute 1.0-ml of the working verification standard to 20-ml with DI water.

8.3.7 CCV, 10.0 mg/l as N: Dilute 2.0-ml of the working verification standard to 20-ml with DI water.

9.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

9.1 The client or other trained personnel collect samples. Samples received at the laboratory are considered representative unless otherwise noted.

9.2 Samples should be collected in a plastic container. Preservation consists of H_2SO_4 and storage in the range of 0.1-6°C. Samples are stored in the reach-in coolers located in the main sample receipt area. Samples that fail to meet the preservation criteria are noted as such on the Cooler Inspection Report in the Login process.

9.3 Analysis must be performed within the maximum allowable hold time of 28 days from collection.

10.0 QUALITY CONTROL

10.1 An *Initial Demonstration of Capability* study must be performed prior to the initial analysis for each analyst and whenever substantial change has occurred in the procedure or instrument. Analyze four separate standards. These standards must be from a source different from that used for calibration and taken through the entire analytical procedure. Submit the data to the QA department for evaluation. Refer to the Capability and Detection Limit Studies SOP for details.

10.2 A *Method Detection Limit* study must be performed for each new procedure, annually thereafter, and whenever a change in instrument occurs. Analyze a minimum of seven (maximum of ten) standards prepared in the range of 2-5 times the latest method detection limit or an estimated detection limit. These standards must be taken through the entire analytical procedure. Submit the data to the QA department for evaluation. Refer to the Capability and Detection Limit Studies SOP for details.

10.3 A *Calibration Verification Standard* must be analyzed immediately after calibration, after every 10 samples, and after the sample. The concentration of the ICV must be different than that of the CCV. Acceptance criteria are 90.0-110% recovery. If acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier. Samples associated with a verification that fails with positive bias can be reported if the sample concentration is a non-detect. ICV and CCV standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier. The reporting of data associated with a failed control sample must be documented with a CAR form.

10.4 A *Calibration Verification Blank* sample must be analyzed after each calibration verification standard. The acceptance criteria are < PQL. Analysis for compliance with our Wisconsin DNR certification must be evaluated down to the current MDL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate. If the blank does not meet the acceptance criteria, all samples < PQL or greater than 10 times the blank contamination may be reported. All other environmental samples must be reanalyzed or reported with an appropriate qualifier in the Case Narrative of the report. The reporting of data associated with a failed control sample must be documented with a CAR form.

10.5 A *Method Blank* must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per day. Acceptance criteria are < PQL. Analysis for compliance with our Wisconsin DNR certification must be evaluated down to the current MDL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate. If the blank does not meet the acceptance criteria, all samples < PQL or greater than 10 times the blank contamination may be reported. All other environmental samples must be reanalyzed or reported with a "B" qualifier, which is automatically applied in the LIMS. The reporting of data associated with a failed control sample must be documented with a CAR form.

10.6 A *Laboratory Control Sample* must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per day. Acceptance criteria are the statistically generated limits of 85.2-112% recovery. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria all environmental samples must be reprepared and analyzed or reported with an appropriate qualifier. If the LCS fails with high bias, samples having a non-detectable concentration may be reported without qualification. LCS's that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.

The reporting of data associated with a failed control sample must be documented with a CAR form.

10.7 A *Matrix Spike and Matrix Spike Duplicate* sample must be prepared and analyzed with each batch of maximum 10 samples and at a minimum of one per day. Acceptance criteria for the MS are the statistically based limits of 72.1-129% recovery with a 16.2 RPD for waters and 89.4-116% recovery with a 14.4 RPD for solids. If the acceptance criteria for either, accuracy or precision are not met, reanalyze. If reanalysis fails to meet the acceptance criteria the sample and its MS/MSD must be reprepared and analyzed or reported with an appropriate qualifier. If the concentration measured in the sample is greater than 4-times the concentration of the spike, the spike amount used is insufficient and the MS/MSD not applicable. MS/MSD's that fail to meet the accuracy criteria are automatically flagged in LIMS with a "S" qualifier. Those failing to meet the precision criteria are automatically flagged in LIMS with a "R" qualifier. The reporting of data associated with a failed control sample must be documented with a CAR form.

10.8 A *Post Digestion Spike* sample may be analyzed to evaluate the source of matrix effects (i.e. MS/MSD failure). Acceptance criteria are 80.0-120% recovery. Regardless of the recovery, report the performance of the PDS on a CAR form. PDS's that fail to meet the accuracy criteria are automatically flagged in LIMS with a "S" qualifier.

11.0 CALIBRATION AND STANDARDIZATION

Calibration data is documented and retained using the printouts from the instrument.

11.1 Perform the required preventative maintenance as necessary.

11.2 Install ammonia manifold on the instrument in the Channel 2 position. Insert 630-nm interference filter into detector module and connect sample loop (13 cm) in injection valve at the 1 and 4 positions. Detach pump tubing at the pump tube adapter on the carrier line. Connect manifold to 650 cm of tubing wrapped around heater block, set for 60 C, allow 15 min for heating unit to warm up. Insert the tubing that is still attached to the manifold into the number 3 position on the injection valve and then attach the tubing from the number 2 position on the valve to remaining carrier line. Attach reagent and sample lines to pump with cassettes and switch on power to the instrument.

11.3 Load autosampler tray with standards and samples.

11.4 Log into Omnion. Open the NH3 method and the NH3 tray.

11.5 Place reagent lines into DI water and pump through manifold until analysis is ready to start at which time the lines are placed into appropriate reagent containers.

11.6 Check for leaks and smooth flow.

11.7 Place the working calibration standard on the autosampler. Calibrate from high to low concentration at 0, 0.100, 0.500, 2.00, 5.00, 10.0, and 20.0 mg/L as N.

11.8 Place reagent transmission lines into the appropriate containers and allow to pump through manifold until a stable baseline is achieved.

11.9 Select Run Tray.

11.10 Check the linearity and replication of the calibration curve. Acceptance criteria are $r \geq 0.995$. If calibration is acceptable, continue with sample analysis. If calibration is not acceptable, recalibrate.

12.0 PROCEDURE

12.1 DISTILLATION

Preparation data is documented and retained using the Ammonia Distillation log (copy attached).

12.1.1 50-ml of 0.04 N H_2SO_4 is poured into a 400-ml beaker and is placed under the condenser unit so as to submerge the outlet of the distillation unit in the solution.

12.1.2 Pour 250-ml of sample and 12.5-ml borate buffer into a distillation flask.

12.1.3 Adjust pH to range of 9 - 10 using NaOH or 1:1 H_2SO_4.

12.1.4 Place the distillation flask on the heating mantel and connect to the condenser unit. Verify the cooling water is turned on.

12.1.5 Turn the heating mantle on "high" and collect slightly less than 250-ml of distillate.

12.1.6 Turn off the heating mantle and collect the remaining drops of distillate.

12.1.7 When no more distillate emerges from the outlet, turn off the cooling water. DO NOT turn off heating mantel while condenser outlet is submerged. cooling of distillation flask will cause a vacuum and will evacuate distillate into distillation flask.

12.1.8 If final volume remains less than the original sample volume, dilute distillate to with reagent water to maintain a 1:1 ratio.

12.2 ANALYSIS

12.2.1 Place samples on the autosampler tray and continue with analysis as described in the Calibration section.

13.0 CALCULATIONS AND DATA HANDLING

13.1 The sample concentration is calculated as follows. Using a 1st Order Polynomial regression (i.e. y = mx+b), the instrument calculates the aqueous concentration based upon the data from the calibration curve.

Conc., ppm = (A) (B) (C) / D

Where: A = aqueous conc., mg/l
B = dilution factor
C = final volume, ml
D = initial sample size, ml or g

13.2 The LIMS calculates the dry-weight concentration for solid samples as follows:

$$\text{Conc. Dry} = \frac{\text{(wet weight conc.)}}{\text{(100 - \%Moisture)}}$$

13.3 After review, enter final results into the LIMS system. Results flagged by the LIMS with an "E" qualifier are above the linear range of the instrument. There is less certainty in these data and, if sufficient sample and holding time are available, should be reanalyzed at an appropriate dilution. Details on the procedure for entering analytical data are in the Data Entry SOP. The peak integration must be performed according to the Manual Integration of Chromatographic Peaks SOP.

14.0 METHOD PERFORMANCE

14.1 Method Detection Limit

The latest MDL study yielded the following data:

n =	8	
Standard Deviation (σ_{n-1})	0.017	mg/l
Spiked Concentration	0.200	mg/l
Average Concentration	0.198	mg/l
Average Recovery	99.3	%
Calculated MDL	0.052	mg/l

14.2 Initial Demonstration of Capability

A typical IDC study will yield data similar to:

n =	4	
Standard Deviation (σ_{n-1})	5.15	mg/l
Spiked Concentration	4	mg/l
Average Concentration	4.19	mg/l
Average Recovery	104.7	%

15.0 POLLUTION PREVENTION

15.1 The quantity of chemicals purchased should be based on expected usage during their shelf life and the disposal cost of unused material.

15.2 Prepare the minimum amount of reagent and standard necessary.

16.0 WASTE MANAGEMENT

16.1 Refer to the SIMALABS International Sample Disposal SOP for guidance on the disposal of any resulting residue, digestate, distillate, extract or standard.

17.0 REFERENCES

17.1 USEPA Method 350.1

17.2 Standard Methods Method 4500-NH_3 G, 18th ED

17.3 Lachat QuikChem Method 10-107-06-1-A

17.4 SIMALABS International Quality Assurance Plan, current revision

18.0 TABLES, FORMS, CHECKLISTS, AND OTHER ATTACHMENTS

Copy of the Ammonia Distillation log

SIMALABS INTERNATIONAL - Merrillville

AMMONIA DISTILLATION - Method 350.1

Batch #: _____ Batch ID: _____ Matrix: Aqueous / Solid

Date/Time: _____ Analyst: _____ Peer Check: _____

	STD / Reagent ID	Expir Date	Conc.
LCS/MSD/MSD			
Borate Buffer			
0.04N H_2SO_4			
NaOH			
H_2SO_4			

	Sample ID	pH Adj. (9-10)	Cont ID	mL / g	MS	MSD	mL Final Vol	Comments
BLK								
STD								
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
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STANDARD OPERATING PROCEDURE FOR CHLORIDE (SILVER NITRATE TITRATION) USING STANDARD METHODS METHOD 4500-Cl^- B AND SW-846 METHOD 9253

Originating Author: Unknown
Revision Author: Jeff Loewe

This SOP is effective upon signed approval by the following:

Troy M. Goehl

Inorganics Manager — Date: 8/24/06

Jeffrey M. Loewe

QA/QC Manager — Date: 8/25/06

DISCLAIMER: This SOP has been developed for use at the Microbac Laboratories, Merrillville, Indiana facility. It is intended for use by trained analysts. As written, this SOP may not be specifically applicable to the activities of other organizations.

Last Review Date:
No Changes Needed
Approved By:

1.0 TABLE OF CONTENTS

2.0 SCOPE AND APPLICATION

2.1 This is a titrimetric procedure for the determination of Chloride. This procedure is applicable to the analysis of aqueous samples as well as the leachates and bomb-combustates from solid samples. The applicable analytes, detection limits and routine reporting limits (PQL) are listed at the Limits tab of the applicable test codes in LIMS.

3.0 SUMMARY

3.1 An aliquot of sample is adjusted to pH 7-9 and titrated with silver nitrate in the presence of potassium chromate. Silver nitrate first reacts selectively with the chloride in the sample to produce insoluble silver chloride then, after the precipitation of all chloride, with the cjromate to form an orange-colored silver chromate precipitate marking the end-point of the titration.

3.2 This procedure is based on the reference methods listed in section 17 of this document. This procedure contains the following deviations from the reference methods.

3.2.1 SW-846 Method 9253 requires two titrations of each sample where the second titration uses exactly one-half of the sample volume used in the initial titration. This procedure does not include this verification step. This is considered a significant deviation and must be reported as a modified procedure when referencing Method 9253.

4.0 DEFINITIONS

4.1 A list of definitions is in the Quality Assurance Plan.

5.0 INTERFERENCES

5.1 Bromide, iodide, and sulfide are titrated along with chloride. Orthophosphate and polyphosphate interfere if present in concentrations greater than 250 and 25 mg/L, respectively.

5.2 Interference from 10 mg/L or more of sulfite can be eliminated with three drops of 30% Hydrogen Peroxide per 100-ml of sample.

5.3 Objectionable color or turbidity must be eliminated.

5.4 Sulfide interference can be removed by adding the contents of one Hach Sulfide Inhibitor reagent pillow to approximately 125-ml sample, mixing for 1-minute then filtering to remove the precipitate.

6.0 SAFETY

6.1 Consult the current revision of the Chemical Hygiene Plan. Requirements for the use of personal protective equipment (e.g. safety glasses, lab coats, gloves) as well as other area-specific safety requirements (e.g. gas cylinders) and MSDS sheets are addressed in the CHP.

7.0 EQUIPMENT AND SUPPLIES

The following is a list of materials needed to perform the steps of this procedure as written. See the reference method(s) for equipment and supply specifications.

7.1 All volumetric glassware used shall be ASTM Class A. Class B glassware must be verified for accuracy on an annual basis and labeled with an appropriate correction.

7.2 pH meter (refer to the pH SOP for details)

7.3 Graduated cylinder or glass pipettes for measuring sample size

7.4 Plastic Solo® cups (alternatively, beakers or conical flasks may be substituted as the titration vessel)

7.5 Stir plate and stir bars

7.6 Burette: 50-ml burette with 0.1-ml graduations and a 10-ml burette with 0.05-ml graduations

8.0 REAGENTS AND STANDARDS

8.1 All reagents used must be analytical reagent (AR) grade or higher. All standards must be traceable to NIST, when available. Certificates of traceability must be obtained from the manufacturer. All reagents and standards must be documented in the appropriate preparation logbook. Refer to the requirements in the Labeling of Standards, Reagents, Digestates and Extracts SOP.

8.2 Reagents

All reagents are stored in the wet chemistry lab unless otherwise noted. Unless otherwise noted, prepared reagents are stored in appropriate plastic containers, retained in the wet chemistry lab and prepared on an as needed basis.

8.2.1 Lab pure water (DI water): Analyte free water is prepared as described in the Quality Assurance Plan. DI water may be obtained from any of the designated taps throughout the lab.

8.2.2 Chloride 2 Indicator Powder Pillows: Hach #1057-66

8.2.3 30% Hydrogen Peroxide: Fisher #H325-500

8.2.4 Sulfide Inhibitor Reagent Powder Pillows: Hach # 2418-99

8.2.5 Sulfuric acid, concentrated: Fisher #A300S-212 or equivalent

8.2.6 Sodium Hydroxide: Fisher #S318-3 or equivalent

8.2.7 Sodium Hydroxide, 1.0N: Dissolve and dilute 40g NaOH to 1L with DI water.

8.2.8 Sodium Chloride (NaCl): Fisher #S271-3 or equivalent. Dry this reagent at 600°C and cool in a dessicator prior to use.

8.3 Standards

All standards are stored in the wet chemistry lab unless otherwise noted.

8.3.1 pH Buffers: Standard buffers of pH 4, 7, and 10. Fisher catalog #SB101-500, SB107-500, and SB115-500, respectively. Equivalent products from other vendors may be substituted. Store these buffers in the main wet chemistry lab.

8.3.2 Silver Nitrate titrant, 0.0141N $AgNO_3$: Fisher catalog LC22600-4 or equivalent. Titrant must be used prior to manufacturer's expiration date.

8.3.3 Stock Verification Standard, 500 mg/L: In a 1L volumetric flask, dissolve and dilute 0.824g of dry NaCl to the mark with DI water. Store this standard in the standards cooler in the main wet chemistry lab.

8.3.4 ICV/LCS, 25 mg/L: Prepare as needed by diluting 5-ml of the stock verification standard to a final volume of 100-ml with DI water.

9.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

9.1 The client or other trained personnel collect samples. Samples received at the laboratory are considered representative unless otherwise noted.

9.2 Samples should be collected in a plastic container. Preservation consists of storage in the range of 0.1-6°C. Samples are stored in the coolers located in the main sample receiving area. Samples that fail to meet the preservation criteria are noted as such on the Cooler Inspection Report in the Login process.

9.3 Analysis must be performed within the maximum allowable hold time of 28-days from collection.

10.0 QUALITY CONTROL

10.1 An *Initial Demonstration of Capability* study must be performed prior to the initial analysis for each analyst and whenever substantial change has occurred in the procedure or instrument. Refer to the Capability and Detection Limit Studies SOP for details.

10.2 A *Calibration Verification Standard* must be analyzed immediately after calibration, after every 10 samples, and after the last sample. In this procedure, these ICV/CCV standards are the same as a Laboratory Control Sample as there is no preliminary sample preparation.

10.2.1 Acceptance criteria are listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier.

10.2.2 ICV and CCV standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.

10.2.3 The reporting of data associated with a failed control sample must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.2.4 Samples associated with a verification that fails with positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.3 A *Calibration Verification Blank* sample must be analyzed after each calibration verification standard. In this procedure, these ICB/CCB standards are the same as a Method Blank as there is no preliminary sample preparation.

10.3.1 The acceptance criteria are < PQL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier.

10.3.2 ICB and CCB standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier. ICB/CCB standards that are below the reporting limit but above the MDL are flagged in LIMS with a "b" qualifier. "b" flagged data is considered as meeting the acceptance criteria.

10.3.3 If the blank does not meet the acceptance criteria, all samples < PQL or greater than 10 times the blank contamination may be reported. All other environmental samples must be reanalyzed or reported with an appropriate qualifier in the Case Narrative of the report. The reporting of data associated with a failed control sample must be documented with a CAR form.

10.4 A *Matrix Spike/Matrix Spike Duplicate* analysis must be performed with each batch of maximum 20 samples per matrix and at a minimum of one per day.

10.4.1 Acceptance criteria are listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria initiate a CAR and report the data set yielding the best precision.

10.4.2 MS/MSD's that fail to meet the accuracy criteria are automatically flagged in LIMS with a "S" qualifier. MSD's that fail to meet the precision criteria are automatically flagged in LIMS with a "R" qualifier.

10.4.3 The reporting of data associated with a failed MS/MSD must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

11.0 CALIBRATION AND STANDARDIZATION

Calibration data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

11.1 Standard titrants are purchased certified from the vendor and do not require re-standardization provided they are used within the vendor-supplied expiration date.

11.2 Perform the required preventive maintenance to the pH meter as necessary.

11.3 Calibrate the pH meter in accordance with the pH SOP.

12.0 PROCEDURE

Analytical data is documented and retained using the Chloride raw data form (copy attached). Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

12.1 Fill a burette with titrant. Dispense any excess titrant so that the volume is at or below the 0-ml graduation.

12.2 Aqueous samples require no preparation. Solid samples must be prepared according to the Water Extraction SOP or by preparing an aqueous extract.

12.2.1 Water samples: Using an appropriate graduated cylinder, transfer a measured volume of sample (default = 100ml) into a titration vessel. If less than 100-ml sample is used, dilute that volume to 100-ml with DI water.

12.2.2 Solid samples: An aqueous extract can be prepared as follows. Dilute 1-10g of sample with 100-ml DI water in a titration vessel or other appropriate container (e.g. beaker). Place a stir bar in the vessel, cover the vessel, place it on a stir plate and stir the sample for a minimum of 2-hours. When the mixing is complete,

filter the extract through a glass fiber filter (or decant the supernatant) for analysis. Enter the ratio of final volume (ml) to sample size (g) as the PFac in LIMS. For example, 2.5g of sample diluted to 100-ml results in a PFac = 40. Document this preparation on the raw data sheet.

12.3 Insert a stir bar, place the vessel on the stir plate and begin stirring the sample.

12.4 Adjust the pH of the sample to pH 7-10 (pH 8.3 is optimum). Additional preparation steps may be necessary as indicated in the Interference section of this SOP.

12.5 Add the contents of one Chloride 2 indicator pillow.

12.6 Read and record the initial volume of titrant in the burette.

12.7 Titrate the sample with Silver Nitrate until color changes from yellow to red-brown then read and record the volume used. NOTE: if the volume of titrant required is more than one burette volume, prepare and analyze a second sample aliquot using a smaller sample size so to minimize any errors of multiple burette readings.

13.0 CALCULATIONS AND DATA HANDLING

13.1 Calculate the sample concentration as follows:

$$\text{Chloride, mg/L} = \frac{(V_{t,\,smp} - V_{t,\,blk})\,(N)\,(35450)}{\text{ml sample}}$$

$$= \frac{(\text{Titrant Volume, ml} - \text{Blank}) * 500}{\text{Sample Volume, ml}}$$

where: $V_{t,\,smp}$ = volume (ml) of titrant used for the sample
$V_{t,\,blk}$ = volume (ml) of titrant used for the ICB

13.2 After review, enter final results into the LIMS system. Results flagged by the LIMS with an "E" qualifier are above the linear range of the instrument. There is less certainty in these data and, if sufficient sample and holding time are available, should be reanalyzed at an appropriate dilution. Details on the procedure for entering analytical data are in the Wet Chemistry Data Entry SOP.

14.0 METHOD PERFORMANCE

14.1 Initial Demonstration of Capability study data and Performance Testing study data are maintained and available from the QA office. The Method Detection Limit is a theoretically calculated concentration; therefore, no MDL study data are available.

15.0 POLLUTION PREVENTION

15.1 The quantity of chemicals purchased should be based on expected usage during their shelf life and the disposal cost of unused material.

15.2 Prepare the minimum amount of reagent and standard necessary.

16.0 WASTE MANAGEMENT

16.1 Refer to the Sample Disposal SOP for guidance on the disposal of any resulting residue, digestate, distillate, extract or standard.

17.0 REFERENCES

17.1 Standard Methods Method 4500-Cl^- B, 18th ED

17.2 SW-846 Method 9253

17.3 Walters, G.L.; et al. Water Analysis Handbook, Hach Company, Loveland, CO 1989

17.4 Microbac Laboratories Quality Assurance Plan, current revision, all sections

18.0 TABLES, FORMS, CHECKLISTS, AND OTHER ATTACHMENTS

Copy of the Chloride raw data form (1 page)
SOP Revision Notification Form with details for this revision

Microbac Laboratories - Chicagoland Division
Chloride - Method 4500ClB

		STD ID / Lot #	Exp. Date	Conc.
Date/Time:	Sodium Chloride:			
Analyst:	$AgNO_3$ (titrant):			0.0141N
Reviewed By/Date:	Chloride 2 Indicator:			

Sample ID	Cont ID	Titrant Start (mL)	Titrant Stop (mL)	Titrant Volume (mL)	Titrant Volume Less Blank (mL)	Sample Volume (mL)	Chloride (mg/L)	Average (mg/L)

Chloride = $\frac{\text{Titrant Volume (mL) - Blank * 500}}{\text{Sample Volume (mL)}}$

Page 1 of 50

Microbac

SOP Revision Notification / Annual Review Form

SOP Name Chloride (Silver Nitrate Titration) SOP ID: Cl-AgNO3(2)

[X] *New Revision* Old Revision # 1 New Revision # 2

Summary of changes:
- 3.2.1 identified deviation to SW-946 Method 9253
- 4.0 removed individual definitions and referenced definitions in QAP
- 7.0 updated equipment list
- 8.1 added reference to requirements of Labeling SOP
- 8.3 added details of pH buffers and ICV/LCS prep
- 10.0 revised format of QC section
- 11.0 reference to pH meter maintenance and calibration SOP
- 11.0 and 12.0 reference to requirements of Document Control SOP
- 12.2 details for solid sample prep
- 18.0 added Raw Data sheet and SOP Revision Notification Form

By signing below, I certify that I have been *notified* about the approval of a *new revision* to the above mentioned SOP. I realize it is *my responsibility* to **read, understand and perform** the procedure as set forth in this new revision.

Initials & Date	Initials & Date	Initials & Date

[ ] *Annual Review* Current Revision # _____

By signing below, I certify that I have **re-read, understand** and **agree to perform** the current revision of the above mentioned SOP

Initials & Date	Initials & Date	Initials & Date

Form revised 01/1998

STANDARD OPERATING PROCEDURE FOR CYANIDE, TOTAL, AMENABLE AND WEAK ACID DISSOCIABLE BY MIDI DISTILLATION AND AUTOMATED COLORIMETRY

Originating Author: Unknown
Revision Author: Troy Goehl

This SOP is effective upon signed approval by the following:

Troy M. Goehl — 4/24/2006

Inorganics Manager — Date

4/24/2006

QA/QC Manager — Date

DISCLAIMER: This SOP has been developed for use at the Microbac Laboratories, Merrillville, Indiana facility. It is intended for use by trained analysts. As written, this SOP may not be specifically applicable to the activities of other organizations.

Last Review Date:
No Changes Needed
Approved By:

1.0 TABLE OF CONTENTS

2.0 SCOPE AND APPLICATION

2.1 This is a manual distillation procedure followed by automated colorimetry for the determination of Cyanide, Total as well as Cyanide, Amenable to Chlorination. This procedure is applicable to the analysis of aqueous, non-aqueous liquid, drinking water, and solid matrix samples. The applicable analytes, detection limits and routine reporting limits (PQL) are listed at the Limits tab of the applicable test codes in LIMS.

3.0 SUMMARY

3.1 Samples are prepared by distillation. In this preparatory step, cyanide is released through acidification as hydrocyanic acid (HCN). This released cyanide is absorbed in a scrubber containing sodium hydroxide. The scrubber solution is then analyzed by automated colorimetry.

3.2 In the automated colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed upon the addition of a pyridine-barbituric acid reagent.

3.3 This procedure is based on the reference methods listed in section 17 of this document. This procedure contains the following deviations from the reference methods.

3.3.1 The reference methods vary in their approaches to interferent removal. This procedure uses ascorbic acid for dechlorination and bismuth nitrate for sulfide removal as these are considered to generate the least amount of "toxic" effects in the resulting waste.

3.3.2 Standard Methods method 4500-CN C results in a distillate matrix of 0.04N sodium hydroxide (section 4a of the method). Although the other reference methods use a 0.25N sodium hydroxide matrix, 4500-CN C has been recognized and accepted as equivalent by various agencies. As such, this procedure is considered in accordance with all the methods referenced in section 17 of this document.

3.3.3 The reference methods vary in their approach to the setups used for distillation. This procedure utilizes a midi-distillation unit, which is a modification to the following methods: EPA 335.2, SW-846 9010B, SW-846 9012A, and the SM 4500-CN series. The sample:reagent ratios and resulting chemistry are equivalent.

4.0 DEFINITIONS

4.1 A list of definitions is in the Quality Assurance Plan.

5.0 INTERFERENCES

5.1 Interferences are eliminated or reduced by distillation.

5.2 Oxidizing agents, such as chlorine, decompose most cyanides.

5.3 Chlorine interferences can be removed by adding an excess of ascorbic acid to the sample prior to distillation.

5.4 Sulfide interference can be removed by adding an excess of bismuth nitrate to the sample before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

5.5 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and/or nitrite will form nitrous acid, which will react with some organic compound to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The interference of nitrate is eliminated by pretreatment with sulfamic acid.

5.6 The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilution of the original scrubber solution to obtain colors of comparable intensity.

6.0 SAFETY

6.1 Consult the current revision of the Chemical Hygiene Plan. Requirements for the use of personal protective equipment (e.g. safety glasses, lab coats, gloves) as well as other area-specific safety requirements (e.g. gas cylinders) and MSDS sheets are addressed in the CHP.

6.2 The distillation and colorimetric phases of this procedure generate toxic forms of cyanide. Care should be taken not to inhale the fumes. The distillation must be performed in a fume hood.

6.3 During the colorimetric procedure, cover the reagent containers with Parafilm® or the container lid to help minimize odors.

7.0 EQUIPMENT AND SUPPLIES

The following is a list of materials needed to perform the steps of this procedure as written. See the reference method(s) for equipment and supply specifications.

7.1 All volumetric glassware used shall be ASTM Class A. Class B glassware must be verified for accuracy on an annual basis and labeled with an appropriate correction.

7.2 Lachat MidiDist™ Distillation System including absorber/reflux tubes, impingers and cold fingers. Kontes #505 or equivalent.

7.3 Vacuum source

7.4 Boiling stones (Fisher, 09-191-12 or equivalent)

7.5 Pipettes, class A glass or adjustable repipettes covering the range to 2-10 ml

7.6 Stir Bar

7.7 Volumetric flask, various sizes

7.8 Balance, top loading

7.9 13 X 100mm disposable borosilicate glass culture tubes

7.10 Lachat FIA system with cyanide manifold 10-204-00-1-A

8.0 REAGENTS AND STANDARDS

8.1 All reagents used must be analytical reagent (AR) grade or higher. All standards must be traceable to NIST. Certificates of traceability must be obtained from the manufacturer. All reagents and standards must be documented in the appropriate preparation logbook. Refer to the requirements in the Labeling of Standards, Reagents, Digestates and Extracts SOP.

8.2 Reagents

Store all reagents in the main wet chemistry lab unless otherwise noted.

8.2.1 Lab pure water (DI water): Analyte free water is prepared as described in the Quality Assurance Plan. DI water may be obtained from any of the designated taps throughout the lab.

8.2.2 Sodium hydroxide (NaOH): Fisher, S318-3 or equivalent

8.2.3 Sodium hydroxide, 1.25N: In a 2L volumetric flask, dissolve and dilute 100g NaOH to the mark with lab pure water.

8.2.4 Sodium hydroxide, 1N: In a 1L volumetric flask, dissolve and dilute 40g NaOH to the mark with lab pure water.

8.2.5 Sulfuric acid, concentrated: Fisher, A300SI-212 or equivalent

8.2.6 Phosphate Buffer, 0.71M: In a 1L volumetric flask, dissolve and dilute to the mark 97g potassium phosphate, monobasic ($KH_2PO_4 \cdot H_2O$) with lab pure water.

8.2.7 Magnesium chloride solution: In a 1L volumetric flask, dissolve and dilute 510g $MgCl_2 \cdot 6H_20$ to the mark with lab pure water. Use Fisher, M33-3 or equivalent.

8.2.8 Sulfamic acid: Use Fisher, A295-100 or equivalent

8.2.9 Bismuth nitrate: Use Fisher, B337-500 or equivalent

8.2.10 Glacial acetic acid: Use Fisher, A507-212 or equivalent

8.2.11 Sodium acetate buffer: In a beaker, dissolve 205g sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$, Fisher #S209-500 or equivalent) in 250-ml lab pure water. When the reagent has dissolved, add glacial acetic acid to pH = 4.5.

8.2.12 Zinc acetate solution: In a beaker, dissolve and dilute 120g zinc acetate dihydrate [$Zn(C_2H_3O_2) \cdot 2H_2O$, Fisher #Z20-500 or equivalent] to 1L with lab pure water.

8.2.13 Methyl Red indicator, Lab Chem LC14120-1

8.2.14 Bismuth nitrate solution: In a 1L volumetric flask, dissolve 30.0g of bismuth nitrate in 100-ml lab pure water. While stirring, add 250-ml glacial acetic acid. Stir until dissolved and dilute to the mark with DI water.

8.2.15 Lead acetate paper (indicator for sulfides): Use Fisher, 14-862 or equivalent

8.2.16 Potassium iodine starch paper (indicator for chlorine).

8.2.17 Calcium Hypochlorite solution, 0.35 M $Ca(OCl)_2$: In a 20-ml volumetric flask, dissolve and dilute 1g of $Ca(OCl)_2$ with lab pure water. Use Fisher, C100-500 or equivalent.

8.2.18 L-Ascorbic Acid: Use Fisher, A61-25 or equivalent.

8.2.19 0.25N NaOH: Dissolve and dilute 20.0g NaOH to a final volume of 2L with DI water.

8.2.20 Chloramine-T: Dissolve 2.0g chloramine-T hydrate in 500-ml deionized water. This reagent must be prepared daily.

8.2.21 Pyridine-Barbituric Acid Reagent: In a 1L volumetric flask, add 15.0g barbituric acid and 100-ml water, rinsing down the sides of the flask to wet the barbituric acid. Add 75-ml pyridine while stirring and mix until the barbituric acid dissolves. Add 15-ml concentrated HCl, mix then allow the solution to cool. Dilute to mark with DI water and invert to mix. Prepare fresh weekly. Store this solution in the reagent storage cooler in the main wet chemistry lab.

8.3 Standards

Store all standards in the standards storage cooler in the main wet chemistry lab.

8.3.1 Stock Calibration Standard, 1000 mg/l: Fisher LC135445-1 or equivalent.

8.3.2 Intermediate Calibration Verification Standard, 5 mg/l: In a 500-ml volumetric flask, dilute 2.5-ml of the stock calibration standard to the mark with 0.25N NaOH. Prepare this standard monthly.

8.3.3 Working Calibration Standard, 0.5 mg/l: In a 50-ml volumetric flask, dilute 5.0-ml of the intermediate calibration standard to the mark with 0.25N NaOH.

8.3.4 Calibration Curve: Using appropriate pipettes, prepare the following standards by diluting the working calibration stock standard with 0.25N NaOH. Preparation can be performed into plastic cups or directly in autosampler vials.

Vol Working Std, ml	Final Vol, ml	Conc, mg/l
1.0	10	0.5
0.5		0.25
0.2		0.1
0.1		005
0.02		0.01
0.01		0.005

8.3.5 Stock Calibration Verification Standard, 1000 mg/l: This standard must be of a separate source or lot number from that used for calibration.

8.3.6 Working Spike Standard, 5 mg/l: In a 500-ml volumetric flask, dilute 2.5-ml of the stock verification standard to the mark with 0.25N NaOH. Prepare this standard monthly.

8.3.7 LCS/MS, 0.2 mg/l: using a volumetric pipette, add 2.0-ml of the working spike standard to 50-ml of DI water or sample to prepare the LCS or MS, respectively.

8.3.8 Working Continuing Calibration Verification (CCV) Standard, 0.20 mg/l: In a 50-ml volumetric flask, dilute 2.0-ml of the working spike standard to the mark with 0.25N NaOH. Prepare this standard daily.

8.3.9 Working Initial Calibration Verification (ICV) Standard, 0.10 mg/l: Make a 1:1 dilution of the CCV standard by diluting equal volumes of the 0.2 mg/L CCV and 0.25N NaOH. Prepare this standard daily.

9.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

9.1 The client or other trained personnel collect samples. Samples received at the laboratory are considered representative unless otherwise noted.

9.2 Aqueous: Samples should be collected in a plastic container having a minimum volume of 100-ml. Preservation consists of NaOH to pH $\geq$ 12 at collection and storage in the range of 0.1-6°C until preparation. Samples are stored in the main walk-in cooler. Solid: Samples should be collected in a plastic or glass container.

Preservation consists of storage in the range of 0.1-6°C until preparation. Samples are stored in the main walk-in cooler.

9.3 Analysis must be performed within the maximum allowable hold time of 14-days from collection.

10.0 QUALITY CONTROL

10.1 An *Initial Demonstration of Capability* study must be performed prior to the initial analysis for each analyst and whenever substantial change has occurred in the procedure or instrument. Refer to the Capability and Detection Limit Studies SOP for details.

10.2 A *Method Detection Limit* study must be performed for each new procedure, semi-annually thereafter, and whenever a change in instrument occurs. Refer to the Capability and Detection Limit Studies SOP for details.

10.3 A *Calibration Verification Standard* must be analyzed immediately after calibration, after every 10 samples, and after the last sample. The concentration of the ICV must be different than that of the CCV.

10.3.1 Acceptance criteria are listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier. NOTE: the criteria specified in EPA 335.4 (for drinking water compliance) is more stringent than that applicable to the other reference methods.

10.3.2 ICV and CCV standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.

10.3.3 The reporting of data associated with a failed control sample must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.3.4 Samples associated with a verification that fails with positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.4 A *Calibration Verification Blank* sample must be analyzed after each calibration verification standard.

10.4.1 The acceptance criteria are < PQL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier. Samples for compliance with our Wisconsin DNR certification must be evaluated down to the current MDL and corrective action taken if the blank exceeds the routine PQL.

10.4.2 ICB and CCB standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.

10.4.3 If the blank does not meet the acceptance criteria, all samples < PQL or greater than 10 times the blank contamination may be reported. All other environmental samples must be reanalyzed or reported with an appropriate qualifier in the Case Narrative of the report. The reporting of data associated with a failed control sample must be documented with a CAR form.

10.5 A *Method Blank* must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per day.

10.5.1 The acceptance criteria are < PQL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier. Samples for compliance with our Wisconsin DNR certification must be evaluated down to the current MDL and corrective action taken if the blank exceeds the routine PQL.

10.5.2 Sample data associated with a MBLK that fails to meet the acceptance criteria are automatically flagged in LIMS with a "B" qualifier. Sample data associated with a MBLK that is detected below the reporting limit but above the MDL are flagged in LIMS with a "b" qualifier. "b" flagged data is considered as meeting the acceptance criteria.

10.5.3 The reporting of data associated with a failed control sample must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.5.4 Samples associated with a MBLK that fails with positive bias can be reported without narration if the sample concentration is < PQL or greater than 10 times the blank contamination.

10.6 A *Laboratory Control Sample* must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per day.

10.6.1 Acceptance criteria are listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier. NOTE: the criteria specified in EPA 335.4 (for drinking water compliance) is more stringent than that applicable to the other reference methods.

10.6.2 LCSs that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.

10.6.3 The reporting of data associated with a failed LCS must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.6.4 Samples associated with a LCS that fails with positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.7 A *Matrix Spike and Matrix Spike Duplicate* sample must be prepared and analyzed with each batch of maximum 10 samples per matrix and at a minimum of one per day.

10.7.1 Acceptance criteria are listed in the appropriate test code in LIMS. (Note: the accuracy criteria have been met provided at least either the MS or MSD meet the %R criteria.) If the acceptance criteria are not met, refer to the MS/MSD Corrective Action Flowchart in the QAP. NOTE: the criteria specified in EPA 335.4 (for drinking water compliance) is more stringent than that applicable to the other reference methods.

10.7.2 MS/MSD's that fail to meet the accuracy criteria are automatically flagged in LIMS with a "S" qualifier. MSD's that fail to meet the precision criteria are automatically flagged in LIMS with a "R" qualifier.

10.7.3 The reporting of data associated with a failed MS/MSD must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.7.4 Samples associated with a MS/MSD that fails the accuracy criteria with positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.7.5 If the concentration measured in the sample is greater than 4-times the concentration of the spike, the spike amount used is insufficient and the MS/MSD not applicable.

10.8 A *Post Digestion Spike* sample should be prepared and analyzed as required by the MS/MSD Corrective Action Flowchart in the QAP.

10.8.1 Acceptance criteria are listed in the appropriate test code in LIMS. If the acceptance criteria are not met, refer to the MS/MSD Corrective Action Flowchart in the QAP.

10.8.2 PDS's that fail to meet the accuracy criteria are automatically flagged in LIMS with a "S" qualifier.

10.8.3 The reporting of data associated with a failed PDS must be documented with a CAR form. If the failure is considered to have a significant affect on

the data, client notification is required using the Case Narrative of the report.

10.8.4 Samples associated with a PDS that fails the accuracy criteria with positive bias can be reported without narration if the sample concentration is below the reporting limit.

11.0 CALIBRATION AND STANDARDIZATION

Calibration data is documented and retained using the printouts from the instrument software. Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

11.1 Perform the required preventative maintenance as necessary. Documentation is retained in the Maintenance Log for the particular instrument used for analysis.

11.2 A new calibration curve must be prepared daily. Prepare the standards for the calibration curve as detailed in the Standards section of this SOP. Verification of the curve is required prior to sample analysis each day of analysis. Analysis of environmental samples cannot proceed without the generation of an acceptable calibration.

11.3 Install Cyanide manifold (reagent lines, interference filter, etc) on the instrument. Set the heater block for 60°C and allow the unit to heat.

11.4 Pump reagents through the system and allow the unit to produce a stable baseline.

11.5 Log into the Omnion software. Open the Cyanide method and tray.

11.6 Load autosampler with standards and samples.

11.7 Select RunTray and calibrate the instrument.

11.8 Using a 1st Order Polynomial regression curve, evaluate the calibration data as follows:

11.8.1 Correlation coefficient must be $r \geq 0.995$. Place a check mark next to the correlation value on the printout to indicate this value has been evaluated.

11.8.2 %RSD of the replicates must be ≤ 14 with the exception of the calibration blank ("0" standard). Place a check mark at the bottom of this column on the printout to indicate this value has been evaluated. Failure of the RSD criteria requires notification to the Unit Supervisor or their designee before the curve may be used (at their discretion).

11.8.3 %Residual of the individual standards must be ≤ 50. Place a check mark at the bottom of this column on the printout to indicate this value has been evaluated. Failure of the Residual criteria requires notification to the Unit

Supervisor or their designee before the curve may be used (at their discretion).

11.8.4 Average area counts of the standards must successively increase/decrease relative to the concentrations of the standards.

11.9 If calibration is not acceptable, recalibrate. If calibration is acceptable, proceed with sample analysis. Analysis of environmental samples cannot proceed without the generation of an acceptable calibration.

12.0 PROCEDURE

Sample preparation is documented using the Cyanide Distillation logbook form (attached). Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

12.1 SAMPLE PRETREATMENT FOR AMENABLE CYANIDE

12.1.1 Transfer a measured portion of sample (50-ml for aqueous samples or approximately 1g with 40-ml of DI water adjusted to pH 11-12 for non-aqueous) into a plastic cup or beaker and stir using stir plate.

12.1.2 Add small amounts of $Ca(OCl)_2$ solution and test sample with potassium iodide (KI) paper until a dark blue stain appears.

12.1.3 Stir treated sample for one hour, checking for chlorine (with KI starch paper) and pH every 15-minutes. If no chlorine is present at time of check (paper stays white), add small amounts of $Ca(OCl)_2$ until positive KI starch test. If the pH varies from 11-12, adjust with acid or base as appropriate.

12.1.4 At the end of the 1-hour stirring period, add $\leq$ 0.1g L-ascorbic acid until chlorine is gone.

12.1.5 Carefully remove the stir bar from the sample and rinse into sample, diluting solid samples to a minimum volume of 50-ml.

12.1.6 Sample is now treated and ready for distillation. NOTE: Two portions (treated and untreated) of the a sample are analyzed to determine Amenable Cyanide. Although it is preferable to have both portions distilled at the same time, it is acceptable to prepare and distill each on separate days (example: Total Cyanide run then later the client requests Amenable; in this example you would not have to run another Total). Also, if the Total Cyanide analysis is complete prior to the preparation/analysis of the treated portion and the Total Cyanide concentration is non-detectable (i.e. <PQL), it is acceptable to forgo the analysis of the treated portion and to report the Amenable Cyanide concentration as non-detectable (i.e. <PQL) as well.

12.2 WEAK ACID DISSOCIABLE

12.2.1 Follow the Sample Distillation procedure below with the following changes.

12.2.1.1 Do not add the sulfamic acid, as NO_2^- and NO_3^- do not interfere.

12.2.1.2 Replace the sulfuric acid and magnesium chloride additions with 4-ml each of the acetate buffer and the zinc acetate solution.

12.2.1.3 After the acetate solutions are added, add 2-3 drops of methyl red indicator and rinse the inlet tube with DI water. If the solution is not pink, add (1+9) acetic acid until the pink color appears and persists.

12.3 SAMPLE DISTILLATION

12.3.1 Place the absorber tubes in the front positions of the digestion block then add 10-ml of 1.25N NaOH and a sufficient volume of DI water so that the water level is near the top of the unit housing.

12.3.2 Test each sample with lead acetate paper for sulfides and with KI paper for chlorine. (Performance of the test paper can be enhanced by wetting the paper with the sodium acetate buffer prior to the sample.) If sulfides are present, the paper will turn dark brown. If the Sulfide check is positive, add 5-ml of bismuth nitrate solution to the reflux tube for that sample. If chlorine is present, the KI paper will generate a line of blue color. If the chlorine check is positive, add $\leq$ 0.1g ascorbic acid to the reflux tube for that sample.

12.3.3 For aqueous samples, transfer 50-ml of sample into a reflux tube (a smaller volume diluted to 50-ml with DI water may be used depending on matrix, concentration or sample availability). For non-aqueous samples, use approximately 1g of sample and 50-ml of water. For amenable cyanide, use the resulting treated sample from the pretreatment procedure.

12.3.3.1 The absorber/reflux tubes (Lachat #71011) are manufactured with a marking at 50-ml. As such, these tubes may be considered volumetric glassware and used as such. If it is determined that the marking on a given piece of glassware is inaccurate, that tube must be replaced or identified in such a way that it is obvious the marking should not be replied upon for volume measurement, in which case a graduated cylinder should be used to measure the volume.

12.3.3.2 Distill solid samples as follows provided they break apart during the distillation process. An inefficient release of the total cyanide may result if the sample remains "clumped together" during the distillation (i.e. surface area is not maximized).

12.3.3.2.1 If it is expected that a solid sample, containing no free liquid, will not break apart during the distillation, perform the pretreatment described in SW-846 Method 9013. Distilling 50-ml of the extract to a final volume of 50-ml results in a PFac = (100 / sample size extracted, g).

12.3.4 Add 0.2g sulfamic acid to each reflux tube. In addition, if the sulfide and/or chlorine checks were positive, add bismuth nitrate and/or ascorbic acid as appropriate.

12.3.5 Add 1-3 boiling stones to each reflux tube. Also, add the spiking standard to the tubes for the LCS, MS and MSD.

12.3.6 On laboratory tape, label the test being done (total or amenable) and the sample number. Place this on the absorber tube of the corresponding sample.

12.3.7 Place a reflux impinger, with the vacuum tubing facing forwards, into each reflux tube.

12.3.8 Place an absorber impinger into each absorber tube and connect the reflux impinger to the corresponding absorber impinger.

12.3.9 Connect the absorber impinger vacuum tube to the valve tube.

12.3.10 Place a cold finger condenser into each reflux impinger ensuring that the connection is tight.

12.3.11 Turn on cold water.

12.3.12 With all the vacuum valves on the digestion block turned off, turn on the vacuum source then turn on each vacuum valve and adjust to a flow rate of approximately three bubbles per second in each reflux tube. This should result in a slight foam on top of the sodium hydroxide solution in the absorber tubes. Do not set the intake rate too high, as this causes NaOH solution in absorber jacket to be evacuated from jacket. (Note: If there is not a foam "head" forming in the absorber tube or no bubbles emerging in the reflux tubes, this is indicative of a vacuum leak.) Check for and correct any loose connections. The intake rate for each set-up may have to be adjusted and re-adjusted until the pressure throughout all 10 set-ups equilibrates.

12.3.13 Slowly and carefully add 2.5-ml of concentrated H_2SO_4 into all inlet holes. CAUTION: Samples may foam up through the inlet holes upon addition of the acid. Rinse inlet hole well with DI water and allow adequate time for the reagent/sample to mix.

12.3.14 Add 2.0-ml of $MgCl_2$ solution into all inlet holes and rinse with water. CAUTION: If inlet hole has not been thoroughly rinsed after the addition of H_2SO_4, a violent reaction may occur inside the inlet hole when $MgCl_2$ is added. Rinse inlet hole well with DI water.

12.3.15 Turn on the power switch of the distillation block. Set the timer for 105-minutes (15-minute warm-up, 90-minute reflux) and allow the samples to distill (units are manufactured to run at 125°C). The unit will automatically shut off the heat upon completion of the timed cycle.

12.3.16 At the completion of the distillation, turn the dial to "off", turn the power switch to "off" and allow the block to cool for a minimum of 15-minutes.

12.3.17 Disassemble the distillation set ups. Wash-down the impinger with DI water collecting this wash in the absorber tube.

12.3.18 In the absorber tube, dilute the distillate with lab pure water to a final volume of 50-ml.

12.3.19 Mix and pour the solution from the absorber tube into a solo cup and tightly place a lid on it. Transfer the label from the absorber tube onto the lid.

12.3.20 Transfer distillates to the Lachat operator for analysis. If distillates are not to be analyzed the same day, store them at 4°C until analyzed.

12.4 ANALYSIS

Analytical data is documented and retained using the instrument printout. Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

12.4.1 Place samples on the autosampler tray and continue with analysis as described in the Calibration section. Samples having a concentration above that of the high calibration standard must be diluted with 0.25N NaOH. Dilutions may be prepared directly in autosampler tubes using appropriate pipettes.

13.0 CALCULATIONS AND DATA HANDLING

13.1 After review, enter final results into the LIMS system. Results flagged by the LIMS with an "E" qualifier are above the linear range of the instrument. There is less certainty in these data and, if sufficient sample and holding time are available, should be reanalyzed at an appropriate dilution. Details on the procedure for entering analytical data are in the Data Entry – Wet Chemistry SOP. The peak integration must be performed according to the Manual Integration of Chromatographic Peaks SOP.

13.2 The instrument calculates the sample concentration using 1st order linear regression based on the calibration curve (i.e. y = mx+b). LIMS calculates the final sample concentrations as follows:

TOTAL or WEAK ACID DISSOCIABLE
CN^-, ppm as N = (A) (B) (C) / D

where: A = concentration measured in mg/l
B = final volume of distillate, ml
C = dilution factor
D = sample size, ml or g

AMENABLE
CN^-, ppm = A – B

where: A = total cyanide concentration, ppm
B = cyanide concentration from treated sample, ppm

13.3 The LIMS calculates the dry-weight concentration for solid samples as follows:

$$\text{Conc. Dry} = \frac{\text{(wet weight conc.)}}{\text{(100 - \%Moisture)}}$$

14.0 METHOD PERFORMANCE

14.1 Initial Demonstration of Capability study data, Method Detection Limit study data and Performance Testing study data are maintained and available from the QA office.

15.0 POLLUTION PREVENTION

15.1 The quantity of chemicals purchased should be based on expected usage during their shelf life and the disposal cost of unused material.

15.2 Prepare the minimum amount of reagent and standard necessary.

15.3 The midi-distillation technique uses less reagent volume and produces less waste than the macro-distillation.

16.0 WASTE MANAGEMENT

16.1 Refer to the Sample Disposal SOP for guidance on the disposal of any resulting residue, digestate, distillate, extract or standard.

16.2 Collect the analysis effluent in a separate container. This effluent contains cyanide and pyridine and is handled separately from general wastes.

17.0 REFERENCES

17.1 USEPA Method 335.2, March 1983

17.2 USEPA Method 335.4, revision 1.0

17.3 SW-846 Methods 9010B, 9012A, and 9013

17.4 Standard Methods Method 4500-CN C, E, G, and I 18th ED.

17.5 Lachat QuikChem Method 10-204-00-1-A, revised 28 August 2000

17.6 Microbac Laboratories Quality Assurance Plan, current revision

18.0 TABLES, FORMS, CHECKLISTS, AND OTHER ATTACHMENTS

Copy of the Cyanide Distillation logbook form (1 page)

Microbac Laboratories - Chicagoland Division
CYANIDE DISTILLATION - Method 9012 / 335.2

Batch #:_____ Batch ID:_____ Matrix: Aqueous / Solid

Date/Time:_____ Analyst:_____ Peer Check:_____

	STD / Reagent ID	Exp. Date	Conc.
LCS/MS/MSD			
NaOH			

	Sample ID	Cont ID	mL / g	MS	MSD	mL Final Volume	Cl_2 check performed	S^{2-} check performed	Comments
PB									
LCS									
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
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revision: d_8-03

Page 1 of 1

STANDARD OPERATING PROCEDURE FOR SULFATE BY EPA METHOD 375.4 AND SW-846 METHOD 9038

Originating Author: Jeff Loewe
Revision Author: Deanna Grieger

This SOP is effective upon signed approval by the following:

Troy Goehl
Unit Supervisor — Date: 2-22-02

Jeffrey M. Loewe
QA/QC Director — Date: 2-22-2002

DISCLAIMER: This SOP has been developed for use at the SIMALABS International, Merrillville, Indiana facility. It is intended for use by trained analysts. As written, this SOP may not be specifically applicable to the activities of other organizations.

1.0 TABLE OF CONTENTS

2.0 SCOPE AND APPLICATION

2.1 This is an automated turbidimetric procedure for the determination of Sulfate. This procedure is applicable to the analysis of aqueous and solid matrix samples. The routine reporting limit (PQL) is 10 mg/l.

2.2 This procedure is also used for the analytical determination of Sulfur by bomb calorimetry.

3.0 SUMMARY

3.1 Sulfate in the sample is converted to barium sulfate via precipitation with barium chloride. The precipitate is suspended as a colloid with gelatin and polyvinyl alcohol. The precipitate scatters at 420-nm to produce a signal proportional to the sulfate concentration.

3.2 The linear working range is 3 – 300 mg/l.

3.3 For the determination of Sulfur, the SO_4^{2-} result is multiplied by a stoichiometric factor to convert from SO_4^{2-} to S.

4.0 DEFINITIONS

4.1 Accuracy – The degree of agreement of a measured value with the true or expected value of the quantity of concern (% recovery of a known spiked analyte).

4.2 Aliquot – A measured portion of a sample, or solution, taken for sample preparation or analysis.

4.3 Analyte – The specific component measured in a chemical analysis. Nitrate and Nitrite are separate analytes applicable to this procedure.

4.4 Analytical Batch – A group of samples which are analyzed, at the instrument level, together using the same method, reagents and apparatus within the same time period. Typically, these are samples in the same batch ID in the LIMS.

4.5 Blank – An artificial sample designed to assess specific sources of laboratory contamination.

- Calibration Blank – An aliquot of water analyzed to verify that the analytical system is free from contamination. As there is no preparation step for aqueous samples, the calibration blank is equivalent to the method blank and may also be referred to as a procedural blank.

4.6 Bias – The deviation of a measured value from a known or accepted value due to matrix effects or method performance. Bias may be determined quantitatively to correct measured values. Bias may be positive or negative.

4.7 Calibration – The establishment of an analytical curve based on the absorbance, response, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type and concentration of acids, solvents, or other solutions used in the sample preparation.

4.8 Continuing Calibration Verification Standard (CCV) – A standard used to verify the continued acceptability of the initial calibration curve. A continuing calibration verification must be after every 10 samples and after the last sample. The concentration of the continuing calibration verification standard shall be varied from that of the initial calibration verification standard.

4.9 Detection Limit – The smallest concentration/amount of some component of interest that can be measured by a single measurement with a stated level of confidence.

- IDL – Instrument detection limit. A statistically determined detection limit used to estimate the instrument's sensitivity. The IDL is obtained by analyzing seven consecutive blanks to assess the variability of the instrument.

- MDL – Method detection limit. The minimum concentration of a substance that can be measured and reported with a 99% degree of confidence. MDLs are determined by analyzing a minimum of seven consecutive standards that have been processed through all preparatory steps.

- PQL – The Practical Quantitation Limit is the lowest concentration that can reliably be achieved within specified limits of precision and accuracy during routine laboratory operating conditions. Typically, the PQL is a value in the range of 5 - 10 times the MDL. This is the routine reporting limit and is also referred to as the Estimated Quantitation Limit (EQL).

4.10 Initial Calibration Verification (ICV) – A standard used to verify the accuracy of calibration standards. Prepared from a second source than that of the calibration standards, its known value is measured against the calibration curve. This determines the integrity of working standards. Also referred to as an external verification standard or check standard. As there is no preparation step for aqueous samples, the ICV is equivalent to the Laboratory Control Sample (LCS).

4.11 Holding Time – The maximum storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

4.12 Matrix – The component or substrate which may contain the analyte of interest. Matrices are limited to the following: aqueous (includes extracts from the TCLP or other extraction procedure, groundwater, surface water, and wastewater), drinking water (potable water and laboratory pure water), non-aqueous liquid (organic liquid having <15% settleable solids), and solid (includes sediment, sludge, and soil).

4.13 Matrix Spike (MS) – An aliquot of a sample that is spiked with a known amount of target analyte(s). Recovery of the matrix spike, expressed as percent recovery, is

used to assess the bias of a method in a given sample matrix. Also referred to as a laboratory fortified sample matrix (LFSM).

4.14 Matrix Spike Duplicate (MSD) – An aliquot of the same sample used for the MS, spiked with the identical amount(s) of target analyte(s) as the MS. Results of the two spikes are used to assess both the bias and precision of a method with a given sample matrix. Also referred to as a laboratory fortified sample matrix duplicate (LFSM DUP).

4.15 Percent Recovery – A measure of accuracy that is calculated as the measured value relative to the true value, expressed as a percent.

$$\%R = \frac{MV}{TV} * 100$$

where: MV = measured value
TV = true value

4.16 Precision – The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions. It is concerned with the comparability of results from duplicate or replicate analyses. (%RPD between the recoveries of two known analyte spikes, and %RSD between the recoveries of three or more measurements).

4.17 Preservative – A reagent added to a sample, or an action used, to prevent or slow decomposition or degradation of a target analyte or a physical process. Thermal and chemical preservation may be used in tandem to prevent sample deterioration.

4.18 Relative Percent Difference (% RPD) – Used to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

$$\%\ RPD = \frac{|X - Y|}{(X + Y) / 2} * 100$$

where: X = value 1
Y = value 2

4.19 Sample – A portion of material to be analyzed.

- Environmental sample – sample supplied by the client for analysis.
- QC sample – sample prepared in the lab analyzed to assess the bias/precision of the analytical system.

5.0 INTERFERENCES

5.1 Color and turbidity will interfere.

5.2 Silicate in excess of 500 mg/l SiO_2/l and large quantities of organic matter will interfere.

5.3 Sulfites and sulfides may oxidize and then precipitate as barium sulfate.

6.0 SAFETY

6.1 Eye protection must be worn at all times while in the laboratory.

6.2 Lab coats and gloves are recommended. Avoid direct contact with reagents, standards, and/or samples.

6.3 Consult the Material Safety Data Sheets (MSDS) for each chemical used for information regarding fire hazard, toxicity, first aid, storage, disposal, spill procedures, and recommended protective equipment.

6.4 Chemicals having the potential to produce toxic fumes must be handled in a fume hood.

7.0 EQUIPMENT AND SUPPLIES

The following is a list of materials needed to perform the steps of this procedure as written. See the reference method(s) for equipment and supply specifications.

7.1 All volumetric glassware used shall be ASTM Class A.

7.2 Volumetric flasks, various sizes

7.3 Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios

7.4 Glass wool

8.0 REAGENTS AND STANDARDS

8.1 All reagents used must be analytical reagent (AR) grade or higher. All standards must be traceable to NIST. Certificates of traceability must be obtained from the manufacturer. All reagents and standards must be documented in the appropriate preparation logbook. Refer to the requirements in the Labeling of Standards, Reagents, Digestates and Extracts SOP.

8.2 Reagents

All reagents are stored in the main wet cooler unless otherwise noted.

8.2.1 Lab pure water. Analyte free water is prepared as described in the Quality Assurance Plan.

8.2.2 Hydrochloric acid, conc. HCl: Fisher catalog #A508-212 or equivalent

8.2.3 Hydrochloric acid, 6N HCl: In a 100-ml volumetric flask, dilute 50-ml conc. HCl to the mark with DI water.

8.2.4 Hydrochloric acid, 0.1N HCl: In a 1L volumetric flask, dilute 16.7-ml 6N HCl to the mark with DI water.

8.2.5 Gelatin: Bloom calf skin gelatin. Aldrich catalog #27,162-4 or equivalent

8.2.6 Polyvinyl alcohol (PVA): 98% hydrolyzed, Acros #9002-89-5 or equivalent

8.2.7 Barium chloride ($BaCl_2$): Fisher catalog #B34-500 or equivalent, $BaCl_2 2H_2O$

8.2.8 Barium chloride solution: *Prepare this solution the day before it is needed. The solution must be slowly cooled to room temperature prior to use. The shelf life of this reagent is 2 days.* In a beaker, place 4.0g gelatin and 40-ml DI water. Allow the mixture to soften for 15 minutes. The water will be completely absorbed by the gelatin. In a separate beaker, mix 1.2g PVA and 100-ml DI water. Stir this solution for 15 minutes. This mixture will not completely dissolve. In a 1L beaker, transfer the PVA mixture (dissolved and undissolved portions) into 800-ml hot DI water. Add the softened gelatin to the hot water and continue to heat and stir the solution until all of the contents are dissolved. This may take up to 1 hour. Dilute the solution to 1L with DI water. Filter the solution through glass wool (pre-rinsed with DI water) into a 1L volumetric flask. Add 50.0g $BaCl_2$ and stir to dissolve. The reagent may be slightly turbid. Allow the reagent to slowly cool to room temperature prior to use.

8.3 Standards

All standards are stored in the main wet chemistry cooler unless otherwise noted.

8.3.1 Sodium sulfate, anhydrous (Na_2SO_4): Fisher catalog #S421-10 or equivalent. Obtain 2 different stocks/lot numbers for the preparation of the calibration and verification stock standards. Dry for 2 hours at 110°C and cool in a desiccator.

8.3.2 Stock Calibration Standard, 1500 ppm as SO_4^{2-}: In a 1L volumetric flask, dissolve and dilute 2.2185g Na_2SO_4 to the mark with DI water.

8.3.3 Working Calibration Standard, 300 ppm as SO_4^{2-}: In a 1L volumetric flask, dilute 200-ml of the stock calibration standard to the mark with DI water. This standard is used for the autosampler to dilute and prepare the calibration curve.

8.3.4 Stock Verification Standard, 1500 ppm as SO_4^{2-}: In a 1L volumetric flask, dissolve and dilute 2.2185g Na_2SO_4 to the mark with DI water. This must be prepared from a source/lot different that that used for calibration.

8.3.5 Intermediate Verification Standard, 300 ppm as SO_4^{2-}: In a 1L volumetric flask, dilute 200-ml of the stock verification standard to the mark with DI water.

8.3.6 ICV, 75.0 ppm as SO_4^{2-}: In a 1L volumetric flask, dilute 50-ml of the stock verification standard to the mark with DI water.

8.3.7 CCV, 150 ppm as SO_4^{2-}: In a 1L volumetric flask, dilute 100-ml of the stock verification standard to the mark with DI water.

8.3.8 MS, 60.0 ppm as SO_4^{2-}: Add 2.0-ml of the intermediate verification standard to 8-ml sample.

9.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

9.1 The client or other trained personnel collect samples. Samples received at the laboratory are considered representative unless otherwise noted.

9.2 Samples should be collected in a plastic container providing a minimum volume of 100-ml. Preservation consists of storage in the range of 0.1-6°C from collection until analyzed. Samples are stored in the main sample storage coolers located in the sample receipt area.

9.3 Analysis must be performed within the maximum allowable hold time of 28 days from collection.

10.0 QUALITY CONTROL

10.1 An *Initial Demonstration of Capability* study must be performed for each analyte prior to the initial analysis for each analyst and whenever substantial change has occurred in the procedure or instrument. Analyze four separate standards prepared in the range of 8-10 times the method detection limit listed in section 14.0. These standards must be from a source different from that used for calibration and taken through the entire analytical procedure. Submit the data to the QA department for evaluation. Refer to the Capability and Detection Limit Studies SOP for details.

10.2 A *Method Detection Limit* study must be performed for each analyte annually and whenever a change in instrument occurs. Analyze a minimum of seven (maximum of ten) standards prepared in the range of 2-5 times the method detection limit listed in section 14.0 or an estimated detection limit. These standards must be taken through the entire analytical procedure. Submit the data to the QA department for evaluation. Refer to the Capability and Detection Limit Studies SOP for details.

10.3 An *Initial Calibration Verification (ICV) Standard* must be analyzed immediately after calibration. Acceptance criteria are the statistical recovery limits of 85.9 – 112%. If acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate. Samples associated with a verification that fails with high bias can be reported if the sample concentration is a non-detect. The LIMS automatically flags ICV results not meeting the acceptance criteria with a "S" qualifier. If insufficient hold time or sample volume remains for reanalysis, complete and submit a Corrective Action Report (CAR) Form and

report the data with a Case Narrative notifying the client of the control failure. Details on statistical limits are in the Generation and Updating of Statistical Recovery Limits SOP.

10.4 A *Continuing Calibration Verification (CCV) Standard* must be analyzed immediately after every 10 environmental samples and after the last sample. Acceptance criteria are the statistical recovery limits of 85.9 – 112%. If acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate. Samples associated with a verification that fails with positive bias can be reported if the sample concentration is a non-detect. The LIMS automatically flags CCV results not meeting the acceptance criteria with a "S" qualifier. If insufficient hold time or sample volume remains for reanalysis, complete and submit a Corrective Action Report (CAR) Form and report the data with a Case Narrative notifying the client of the control failure. Details on statistical limits are in the Generation and Updating of Statistical Recovery Limits SOP.

10.5 A *Calibration Verification Blank (ICB/CCB)* sample must be analyzed after each calibration verification standard. The acceptance criteria are < PQL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate. If the blank does not meet the acceptance criteria, all samples < PQL or greater than 10 times the blank contamination may be reported. The LIMS automatically flags blank results not meeting the acceptance criteria with a "B" qualifier. If insufficient hold time or sample volume remains for reanalysis, complete and submit a Corrective Action Report (CAR) Form and report the data with a Case Narrative notifying the client of the control failure.

10.6 A *Matrix Spike and Matrix Spike Duplicate (MS/MSD)* sample must be analyzed with each batch of maximum 10 samples and at a minimum of one per day. Acceptance criteria are the statistical limits of 72.0 – 107% recovery and 10.1% RPD. If the acceptance criteria for either, accuracy or precision, are not met, reanalyze. If reanalysis fails to meet the acceptance criteria the sample and its MS/MSD must be reprepared and analyzed or reported with an appropriate qualifier. The LIMS automatically flags MS/MSD results with a "S" qualifier for not meeting the accuracy criteria and with a "R" qualifier for not meeting the precision criteria. If insufficient hold time or sample volume remains for reanalysis, complete and submit a Corrective Action Report (CAR) Form and report the data with a Case Narrative notifying the client of the control failure. Details on statistical limits are in the Generation and Updating of Statistical Recovery Limits SOP.

11.0 CALIBRATION AND STANDARDIZATION

Calibration data is documented and retained using the printouts from the instrument software.

11.1 Perform the required preventative maintenance as necessary.

11.2 Install sulfate manifold on the instrument in the Channel 2 position. Place the 420-nm interference filter into detector module and connect sample loop (100-cm) in

injection valve at the 1 and 4 positions. Detach pump tubing at the pump tube adapter on the carrier line. Insert the tubing that is still attached to the manifold into the number 3 position on the injection valve and then attach the tubing from the number 2 position on the valve to remaining carrier line. Attach reagent and sample lines to pump with cassettes and switch on power to the instrument. (A copy of the flow diagram is included in the Lachat QuikChem™ method.)

11.3 Load autosampler tray with standards and samples.

11.4 Log into Omnion. Open the appropriate method and tray.

11.5 Place reagent lines into DI water and pump through manifold until analysis is ready to start at which time the reagent lines placed into appropriate reagent containers.

11.6 Check for leaks and smooth flow.

11.7 Place the working calibration standard on the autosampler. Calibration must be performed each day of use. Calibrate from high to low concentration at 300, 150, 75, 30, 9, 3, and 0 mg/l. At a minimum, the calibration curve must consist of a blank plus 3 standards, the lowest of which must be at or below the PQL.

11.8 Place reagent transmission lines into the appropriate containers and allow to pump through manifold until a stable baseline is achieved.

11.9 Select Run Tray.

11.10 Check the linearity and replication of the calibration curve. Acceptance criteria are $r \geq 0.995$. If calibration is acceptable, continue with sample analysis. If calibration is not acceptable, recalibrate.

12.0 PROCEDURE

Analytical data is documented and retained using the printouts from the instrument software.

12.1 PREPARATION

12.1.1 Aqueous samples require no preparation. Solid samples must be prepared according to the Water Extraction SOP or by preparing an aqueous extract.

12.1.1.1 To prepare an aqueous extract, dilute 2-10g of sample with 100-ml DI water in a plastic beaker. Place a stir bar in the beaker, cover the beaker, place it on a stir plate and stir the sample for a minimum of 2 hours. When the mixing is complete, filter the extract through a glass fiber filter (or decant the supernatant) for analysis. Enter the ratio of final volume (ml) to sample size (g) as the PFac in the LIMS. For example, 2.5g of sample diluted to 100-ml results in a PFac = 40. Document this preparation on the instrument printout.

12.2 ANALYSIS

12.2.1 Continue with analysis as described in the Calibration section.

13.0 CALCULATIONS AND DATA HANDLING

13.1 This procedure uses a non-linear, multi-segment calibration curve. Using the calibration curve data, the instrument calculates the sample concentration using 3rd Order Polynomial regression [$y = (m_1x^3) + (m_2x^2) + (m_3x) + b$], where m_1 is the slope of segment 1, m_2 is the slope of segment 2, etc. The final sample concentration is calculated as follows:

AQUEOUS SULFATE
SO_4^{2-}, mg/l = (A) (DF)

where: A = concentration measured in mg/l
DF = dilution factor

NON-AQUEOUS SULFATE CONCENTRATION
mg/kg as SO_4^{2-} = (A) (DF) (PFac)

where: A = concentration measured in mg/l
DF = dilution factor at instrument
PFac = extract ratio of final volume (ml) to sample size (g)

SULFUR BY BOMB CALORIMETRY
mg/kg as S = (A) (DF) (PFac) (0.3338)

where: A = concentration measured in mg/l as SO_4^{2-}
DF = dilution factor at instrument
PFac = bomb digest ratio of final volume (ml) to sample size (g)
0.3338 = percentage of S in SO_4^{2-} (33.38%) entered in the conversion field at data entry

13.2 The LIMS calculates the dry-weight concentration for solid samples as follows:

$$\text{Conc. Dry} = \frac{\text{(wet weight conc.)}}{\text{(100 - \%Moisture)}}$$

13.3 Results flagged by the LIMS with an "E" qualifier are above the linear range of the instrument. As there is less certainty in these data the sample should be reanalyzed at an appropriate dilution. Details on the procedure for entering analytical data are in the Data Entry SOP. The peak integrations must be performed according to the Manual Integration of Chromatographic Peaks SOP.

14.0 METHOD PERFORMANCE

14.1 Method Detection Limit

The latest MDL study yielded the following data:

n =	7	
Standard Deviation (σ_{n-1})	0.302	mg/l
Spiked Concentration	10.0	mg/l
Average Concentration	7.73	mg/l
Average Recovery	77.3	%
Calculated MDL	0.95	mg/l

15.0 POLLUTION PREVENTION

15.1 The quantity of chemicals purchased should be based on expected usage during their shelf life and the disposal cost of unused material.

15.2 Prepare the minimum amount of reagent and standard necessary.

16.0 WASTE MANAGEMENT

16.1 Refer to the SIMALABS International Sample Disposal SOP for guidance on the disposal of any resulting residue, digestate, distillate, extract or standard.

17.0 REFERENCES

17.1 USEPA Method 375.4, 1978, MCAWW 1983

17.2 SW-846 Method 9038

17.3 Lachat QuikChem Method 10-116-10-1-E

17.4 SIMALABS International Quality Assurance Plan, current revision

18.0 TABLES, FORMS, CHECKLISTS, AND OTHER ATTACHMENTS

None